chapter

16 Equilibrium in Acid–Base Systems

In this chapter

- Exploration: Salty Acid or Acidic Salt?
- Lab Exercise 16.A: The Chromate–Dichromate Equilibrium
- Web Activity: Edgar Steacie
- Investigation 16.1: Creating an Acid–Base Strength Table
- Lab Exercise 16.B: Predicting Acid–Base Equilibria
- Web Activity: Pool Chemistry
- Lab Exercise 16.C: Aqueous Bicarbonate Ion Acid–Base Reactions
- Investigation 16.2: Testing Brønsted–Lowry Reaction Predictions
- Lab Exercise 16.D: Creating an Acid–Base Table
- Case Study: Changing Ideas on Acids and Bases—The Evolution of a Scientific Theory
- Web Activity: Titration of Polyprotic Acids and Bases
- Biology Connection: Homeostasis
- Web Activity: Preparation of Buffer Solutions
- Web Activity: Maud Menten
- Investigation 16.3: Testing a Buffer Effect

The nature of science involves constant questioning and testing of theories—and so it is with theories about acids and bases. A great many chemical reaction systems involve acids in some way, including the one that begins the decomposition (digestion) of the food you eat, and, thus provides you with energy. Many other types of aqueous reaction systems have rates that are easily controlled by adjusting the level of acidity. Because such systems are commonly found both in nature and in industry, scientists seek to work with the most complete and successful acid–base concepts—which in turn means seeking new ways to test previously accepted theories. Theories that do not describe, explain, and predict the chemistry of acids and bases well enough will initially be restricted to only those situations where they work. As a result of further testing, scientists will either revise the theory, or replace it altogether.

This chapter presents new hypotheses, evidence, and analyses to help you develop a more comprehensive understanding of both the aqueous reaction environment, and the activity of acids and bases within that environment. Your knowledge of chemical equilibrium (Chapter 15) allows you to explore these questions from a new perspective, and, in turn, will allow you to form a more complete and less restrictive theory of acids and bases. In fact, few topics in chemistry illustrate this scientific principle of ongoing theory testing and development so well.

These underlying principles—that theories must be supported by evidence, and that understanding is increased by always questioning and testing existing knowledge—are the basis of the uniquely productive "way of knowing" about the natural world that we call science. To these principles, and to the enormous accumulation of knowledge they have made possible, we owe most aspects of our present technological civilization.

STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. How can some substances neutralize *both* acids and bases?
2. Can acid–base reactions and their products be predicted? Explain.
3. Can pH curves for titrations of weak acids and weak bases predict equivalence points as strong acid–strong base pH curves do? Explain.
4. How is the buffering of some medications related to stomach fluid acidity?

Career Connection:
Environmental Engineer; Chemistry Researcher; Microbiologist

Figure 1
Testing your concepts is a continual part of "doing" science.

Exploration — Salty Acid or Acidic Salt?

In Chapter 5, you learned about saturated solutions as examples of dynamic equilibrium, and prepared a saturated sodium chloride solution. The strong acid, HCl(aq), shares half of its chemical formula with NaCl(aq). How might the two solutions interact?

Materials: two 10 mL graduated cylinders; saturated sodium chloride solution, NaCl(aq); concentrated hydrochloric acid, HCl(aq)

(a) Write and balance a chemical reaction equation for any reaction you can predict when sodium chloride solution and concentrated hydrochloric acid are mixed.

(b) Write an equation to express the nature of a saturated sodium chloride aqueous solution as a dynamic equilibrium.

(c) Write the equilibrium law expression for a saturated aqueous sodium chloride solution. Identify the substance with a constant concentration.

Hydrochloric acid is corrosive. Wear appropriate eye protection, lab gloves, and a lab apron.

- Measure approximately 8 mL of saturated sodium chloride solution into the larger graduated cylinder.
- Measure approximately 2 mL of concentrated hydrochloric acid into the smaller graduated cylinder.
- Pour the concentrated hydrochloric acid into the cylinder containing the saturated sodium chloride solution. Record your observations.
- Dispose of all substances down the sink, using lots of water.

(d) Explain what has apparently happened to the saturated NaCl(aq) equilibrium.

(e) Explain which ion concentration in the large cylinder *must* have changed, whether it was increased or decreased, and what principle you use to "know" this answer.

(f) Which initial solution was more concentrated? Use Le Châtelier's principle to explain how you "know" this answer.

(g) Was the initial HCl(aq) a saturated solution? Was it at equilibrium? Was it at equilibrium before being removed from its closed storage container? Explain how you can use the basic principles of equilibrium to "know" these answers.

16.1 Water Ionization and Acid–Base Strength

Figure 1
The chromate–dichromate aqueous ion system, in equilibria at high and low pH

In many of the preceding units, you have studied examples of chemical reactions and systems that in some way depend on the nature of acids and bases and/or the pH of solution. For example, aqueous permanganate ions are powerful oxidizing agents, but can act to oxidize other reagents only in the presence of hydrogen (hydronium) ions. Almost any soluble R–COOH organic compound will make an aqueous solution with a pH below 7, because the hydrogen atom of such a group is relatively easily removed. The electrolysis of potassium iodide solution produces a solution that is strongly basic. Understanding these connections involves considering equilibrium effects, as shown by the chromate–dichromate aqueous ion system (**Figure 1**).

You have already learned several concepts about the strengths and properties of acids and bases (see Chapter 6 Summary, page 262). If we now combine equilibrium concepts with these acid–base concepts, we can develop a much more comprehensive understanding of acids and bases. This understanding, in turn, will allow you to better explain and predict how acids and bases behave. For instance, the reaction examined in Lab Exercise 16.A is an easily explained example of how the acidity of a solution can directly affect other ion equilibria.

LAB EXERCISE 16.A

The Chromate–Dichromate Equilibrium

In an aqueous solution, chromate ions are in equilibrium with dichromate ions (Figure 1).

$$2\,CrO_4^{2-}(aq) + 2\,H^+(aq) \rightleftarrows Cr_2O_7^{2-}(aq) + H_2O(l)$$

Complete the Prediction and Design (including diagnostic tests) of the investigation report.

Report Checklist

○ Purpose	● Design	○ Analysis
○ Problem	○ Materials	○ Evaluation
○ Hypothesis	○ Procedure	
● Prediction	○ Evidence	

Purpose

The scientific purpose of this investigation is to test a Design for varying the acidity of an equilibrium.

Problem

How does changing the hydrogen ion concentration affect the chromate–dichromate equilibrium?

Hypothesis

The position of this equilibrium depends on the acidity of the solution.

Learning Tip

For discussing acid–base reactions involving weak acids or bases, or when comparing acid or base strengths in aqueous solution, it is normally necessary to represent the "hydrogen" ion as a "hydronium" ion, $H_3O^+(aq)$. Chapter 16 will use this ion representation exclusively, from this point on.

For simplicity, a great many chemical reaction equations use $H^+(aq)$ to represent an aqueous hydrogen ion. This representation often works very well, as in the redox equations used in Unit 7, or the titration analysis equations used for stoichiometric calculations in Chapter 8. For other purposes, however, it is necessary to represent this ion more accurately in order to understand and explain the theoretical nature of the reaction. As you learned in Chapter 6, it is more consistent with evidence to think of this entity as a hydronium ion, and to represent it as $H_3O^+(aq)$. Acid–base equilibrium theory necessarily involves collision–reaction theory for a variety of entities. This chapter will, therefore, use the hydronium ion convention almost exclusively. Before aqueous acidic or basic solution equilibrium can be investigated further, the equilibrium nature of the ions of the solvent (water) must first be examined, understood, and taken into consideration.

The Water Ionization Constant, K_w

Even highly purified water has a very slight conductivity that is only observable if measurements are made with very sensitive instruments (**Figure 2**). According to Arrhenius' theory, conductivity is due to the presence of ions (**Figure 3**). Therefore, the conductivity observed in pure water must be the result of ions produced by the ionization of some water molecules into hydronium ions and hydroxide ions. Because the conductivity is so slight, the equilibrium at SATP must greatly favour the water molecules.

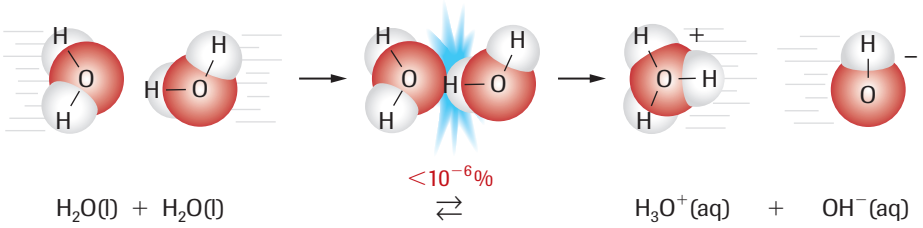


Figure 3
Collisions of water molecules very occasionally produce this cation–anion pair.

$$K_c = \frac{[H_3O^+(aq)][OH^-(aq)]}{\cancel{[H_2O(l)][H_2O(l)]}} \quad \text{or} \quad K_c = [H_3O^+(aq)]\,[OH^-(aq)]$$

Evidence indicates that, at 25 °C, at any given moment, fewer than two of every billion molecules in pure liquid water exist in ionized form! When we write an equilibrium constant expression for this ionization, the value of K_c is an extremely small number. Recall that, because pure liquid water (or the water in any dilute aqueous solution) has an essentially constant concentration, it does not appear in the expression; it is simply incorporated into the equilibrium constant value.

The water ionization equilibrium relationship is so important in chemistry that this particular K_c constant is given its own special symbol and name. This new constant is called the ion product or **ionization constant for water, K_w**.

$$K_w = [H_3O^+(aq)][OH^-(aq)] = 1.00 \times 10^{-14} \text{ at SATP}$$

The equilibrium equation for the ionization of water shows that hydronium ions and hydroxide ions form in a 1:1 ratio. Therefore, the concentration of hydronium ions and hydroxide ions in pure water must be equal. This equality must also be true for any neutral aqueous solution. Using the mathematical expression for K_w, and the value of K_w at SATP, the concentrations of $H_3O^+(aq)$ and $OH^-(aq)$ can be calculated by taking the square root of the K_w value. Recall (from Chapter 15) that in all entity concentration calculations from any K_c value, the entity concentration is simply assumed to have units of mol/L.

$$[H_3O^+(aq)] = [OH^-(aq)] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ mol/L}$$

The ionization of water is especially important in the empirical and theoretical study of acidic and basic solutions. Recall from Chapter 6 that, according to the modified Arrhenius theory, an acid is a substance that reacts with water to produce hydronium ions. The additional hydronium ions provided by the acid increase the hydronium ion concentration. Since the hydronium ion concentration is greater than 10^{-7} mol/L, the solution is *acidic*. A *basic* solution is one in which the hydroxide ion concentration is greater

Figure 2
A sensitive multimeter is required to detect the electrical conductivity of the highly purified water that is typically used in a chemistry laboratory. (See Appendix C.3 for guidance on using a multimeter.)

DID YOU KNOW ?

Successful Collisions

A collision that successfully forms hydronium and hydroxide ions is very rare. This is not because *collisions* are rare—each water molecule collides with others tens of trillions of times every second! But, the chance that any given collision will both have sufficient energy, and also be at exactly the right orientation, is very, very small indeed. Ordinarily, an equilibrium so strongly favouring the reverse reaction would just be ignored—thought of as not happening at all—but, in this case, the ions are uniquely important because of the effects they have on all reactions in aqueous solution.

Conversely, you already know that the reverse reaction (hydronium ions with hydroxide ions) is quantitative. Almost every such ion collision will be effective because the required energy is very low, and the attraction of opposite ion charges acts to orient the entities correctly.

Modelling water molecules this way—as space-filling models with superimposed atomic symbols and lines to represent bonds—gives an overall representation of the process that is logically consistent with experimental evidence.

than 10^{-7} mol/L. Basic solutions are produced in two ways: either by the complete dissociation (upon dissolving in water) of an ionic hydroxide, or by partial reaction of some weak base entity (ion or molecule) with water to produce hydroxide ions.

The most important point about K_w is that it applies to pure water, and also to any solution that is mostly water. This means that this ionization equilibrium will be involved in any other reaction going on in aqueous solution, if that reaction involves hydronium ions or hydroxide ions in any way. As an example, consider the equilibrium reaction just studied in Lab Exercise 16.A. Since that reaction involves hydronium (hydrogen) ions, the chromate–dichromate equilibrium can be controlled (shifted) easily, simply by adjusting either the hydronium ion or the hydroxide ion concentration; which really just means deliberately shifting the water ionization equilibrium. A great many chemical reactions are dependent in this way on the water ionization equilibrium. Many of them (those containing $H_3O^+(aq)$ or $OH^-(aq)$ ions) are evident in the Relative Strengths of Oxidizing and Reducing Agents table (Appendix I).

Note that, since the mathematical relationship is simple, we can easily use K_w to calculate either the hydronium ion amount concentration or the hydroxide ion amount concentration in an aqueous solution, if the other concentration is known.

Since $[H_3O^+(aq)][OH^-(aq)] = K_w$

then $[H_3O^+(aq)] = \dfrac{K_w}{[OH^-(aq)]}$

and $[OH^-(aq)] = \dfrac{K_w}{[H_3O^+(aq)]}$

In ordinary dilute aqueous acidic or basic solutions, the presence of substances other than water decreases the certainty of the K_w value at 25 °C to two significant digits.

All questions and examples in this text assume temperatures of 25 °C, and aqueous solutions that are not highly concentrated, with a K_w value of 1.0×10^{-14}, unless specifically stated otherwise.

Learning Tip

Keep in mind that the value for K_w is subject to the same restrictions as any other equilibrium constant: one being that it will change if the temperature changes. For example, in pure water at 20 °C, K_w has a numerical value of 6.76×10^{-15}, whereas at 30 °C its value is 1.47×10^{-14}.

K_w will also change enough to be invalid in any aqueous solution with a very high solute concentration—because then the assumption that the concentration of the water solvent is at or near a constant value (55.5 mol/L) no longer holds true.

CAREER CONNECTION

Environmental Engineer

Monitoring and protecting water quality is an essential part of the work of environmental engineers. They design systems and treatment processes that control pH levels, temperature, and amounts of dissolved oxygen for industries that use water.

Would you like to become an environmental engineer? Look into salaries, employment opportunities, and educational programs at at least two different educational institutions.

www.science.nelson.com GO

Learning Tip

These communication examples show the application of the usual units convention for simplifying calculations from equilibrium constants. Units for the constant are ignored, and other concentration units are always entered in mol/L. Then, since the units for the calculated value are always mol/L, they are just written in with the answer.

COMMUNICATION example 1

A 0.15 mol/L solution of hydrochloric acid at 25 °C is found to have a hydronium ion concentration of 0.15 mol/L. Calculate the amount concentration of the hydroxide ions.

Solution

$HCl(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + Cl^-(aq)$

$$[OH^-(aq)] = \frac{K_w}{[H_3O^+(aq)]}$$

$$= \frac{1.0 \times 10^{-14}}{0.15 \text{ mol/L}} \text{ (entity concentration units assumed to be mol/L)}$$

$$= 6.7 \times 10^{-14} \text{ mol/L}$$

Using the K_w relationship, the hydronium ion concentration is 6.7×10^{-14} mol/L.

COMMUNICATION example 2

Calculate the amount concentration of the hydronium ion in a 0.25 mol/L solution of barium hydroxide.

Solution

$$Ba(OH)_2(s) \longrightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$$

$$[OH^-(aq)] = 2 \times [Ba(OH)_2(aq)]$$
$$= 2 \times 0.25 \text{ mol/L}$$
$$= 0.50 \text{ mol/L}$$

$$[H_3O^+(aq)] = \frac{K_w}{[OH^-(aq)]}$$
$$= \frac{1.0 \times 10^{-14}}{0.50 \text{ mol/L}}$$
$$= 2.0 \times 10^{-14} \text{ mol/L}$$

Using the K_w relationship, the hydronium ion concentration is 2.0×10^{-14} mol/L.

COMMUNICATION example 3

Determine the hydronium ion and hydroxide ion amount concentrations in 500 mL of an aqueous solution for home soap-making containing 2.6 g of dissolved sodium hydroxide.

Solution

$$n_{NaOH} = 2.6 \text{ g} \times \frac{1 \text{ mol}}{40.00 \text{ g}} = 0.065 \text{ mol}$$

$$[NaOH(aq)] = \frac{0.065 \text{ mol}}{0.500 \text{ L}} = 0.13 \text{ mol/L}$$

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

$$[OH^-(aq)] = [NaOH(aq)] = 0.13 \text{ mol/L}$$

$$[H_3O^+(aq)] = \frac{K_w}{[OH^-(aq)]}$$
$$= \frac{1.0 \times 10^{-14}}{0.13 \text{ mol/L}}$$
$$= 7.7 \times 10^{-14} \text{ mol/L}$$

Using the K_w relationship, the hydronium ion concentration is 7.7×10^{-14} mol/L, and the hydroxide ion concentration is 0.13 mol/L.

DID YOU KNOW?

Warnings on Packaging

Many households, in previous centuries, kept supplies of lye (sodium hydroxide) on hand for making soap. Because it looked like sugar, it was occasionally swallowed by curious children, causing terrible injuries to their throats. A prominent American physician, Dr. Chevalier Jackson (1865–1958) realized that warnings on the packaging would encourage parents to keep this dangerous substance out of the reach of their children. This is one of the earliest instances of warning labelling on packaging. Partially because of Dr. Jackson's efforts, the United States Congress passed the Federal Caustic Labelling Act in 1927. In Canada, we have the Consumer Chemicals and Containers Regulations.

Figure 4
Many solutions sold for cleaning windows contain ammonia.

COMMUNICATION example 4

Calculate the amount concentration of hydronium ions in a 0.100 mol/L aqueous solution of ammonia that is used in a spray bottle for window cleaning solution (**Figure 4**). A reference states that there is 2.1% reaction of dissolved ammonia with water (ionization) at this concentration, at SATP.

Solution

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

$$[OH^-(aq)] = \frac{2.1}{100} \times 0.100 \text{ mol/L}$$

$$= 0.0021 \text{ mol/L}$$

$$[H_3O^+(aq)] = \frac{K_w}{[OH^-(aq)]}$$

$$= \frac{1.0 \times 10^{-14}}{0.0021 \text{ mol/L}}$$

$$= 4.8 \times 10^{-12} \text{ mol/L}$$

Using the K_w relationship, in 0.100 mol/L aqueous ammonia, the hydronium ion concentration is 4.8×10^{-12} mol/L.

Practice

1. The hydronium ion concentration in an industrial effluent is 4.40 mmol/L. Determine the concentration of hydroxide ions in the effluent.
2. The hydroxide ion concentration in a household cleaning solution is 0.299 mmol/L. Calculate the hydronium ion concentration in the cleaning solution.
3. Calculate the hydroxide ion amount concentration in a solution prepared by dissolving 0.37 g of hydrogen chloride in 250 mL of water.
4. Calculate the hydronium ion amount concentration in a saturated solution of calcium hydroxide (limewater) that has a solubility of 6.9 mmol/L.
5. What is the hydronium ion amount concentration in a solution made by dissolving 20.0 g of potassium hydroxide in water to form 500 mL of solution?
6. Calculate the percent ionization of water at SATP. Recall that 1.000 L of water has a mass of 1000 g.

Communicating Concentrations: pH and pOH

Recall (Chapter 6) that the enormous range of aqueous solution hydronium ion concentrations is more easily expressed using the logarithmic pH scale (**Figure 5**). Mathematically,

$$pH = -\log [H_3O^+(aq)] \text{ and, inversely, } [H_3O^+(aq)] = 10^{-pH}$$

For basic solutions, it is sometimes more useful to use a scale based on the amount concentration of hydroxide ions. Recall that the definition of pOH follows the same format and the same certainty rule as pH.

$$pOH = -\log[OH^-(aq)] \text{ and, inversely, } [OH^-(aq)] = 10^{-pOH}$$

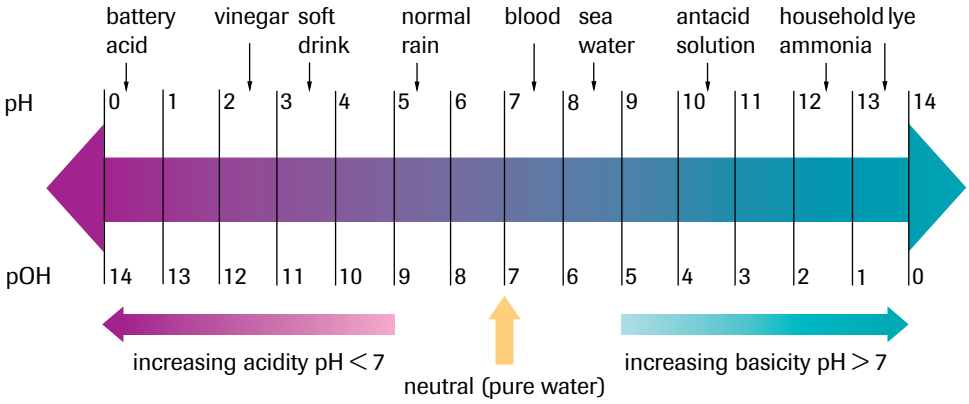


Figure 5
The pH scale

The mathematics of logarithms allows us to express a simple relationship between pH and pOH. According to the rules of logarithms,

$$\log(ab) = \log(a) + \log(b)$$

Using the equilibrium law for the ionization of water,

$$[H_3O^+(aq)][OH^-(aq)] = K_w$$

$$\log[H_3O^+(aq)] + \log[OH^-(aq)] = \log(K_w)$$

$$(-\text{pH}) + (-\text{pOH}) = -14.00$$

$$\text{pH} + \text{pOH} = 14.00 \qquad \text{(at SATP)}$$

This relationship allows for a quick conversion between pH and pOH values.

SUMMARY Water Ionization Conversions and Values (at SATP)

$$K_w = [H_3O^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$$

$$\text{pH} = -\log[H_3O^+(aq)] \qquad \text{pOH} = -\log[OH^-(aq)]$$

$$[H_3O^+(aq)] = 10^{-\text{pH}} \qquad [OH^-(aq)] = 10^{-\text{pOH}}$$

$$\text{pH} + \text{pOH} = 14.00$$

Learning Tip

Recall this convenient "rule of thumb" for keeping track of significant digits in (logarithmic) calculations of pH or pOH.

The number of digits following the decimal point in the pH or pOH (logarithm) value should be equal to the number of significant digits shown in the amount concentration of the ion.

For example, a hydronium ion concentration of 2.7×10^{-3} mol/L is expressed as a pH of 2.57, and a pOH of 4.3 is expressed as a hydroxide ion concentration of 5×10^{-5} mol/L.

Practice

7. Food scientists and dieticians measure the pH of foods when they devise recipes and special diets.

(a) Copy and complete **Table 1**.

Table 1 Acidity of Foods

Food	$[H_3O^+(aq)]$ (mol/L)	$[OH^-(aq)]$ (mol/L)	pH	pOH
oranges	5.5×10^{-3}			
asparagus				5.6
olives		2.0×10^{-11}		
blackberries				10.6

(b) Based on pH only, predict which of the foods would taste most sour.

8. To clean a clogged drain, 26 g of sodium hydroxide is added to water to make 150 mL of solution. What are the pH and pOH values for the solution?

9. What mass of potassium hydroxide is contained in 500 mL of solution that has a pH of 11.5? Comment on the degree of certainty of your answer.

Acid Strength as an Equilibrium Position

In Chapter 6, you learned that acidic solutions of different substances at the same concentration do not possess acid properties to the same degree. The pH of a 1.00 mol/L solution of an acid can vary anywhere from a value of nearly 7 to a value of nearly 0, depending on the specific acid in the solution. Other properties can also vary. For example, acetic acid does not conduct an electric current nearly as well as hydrochloric acid of equal concentration (**Figure 6**). When we observe chemical reactions of these acids, it is apparent that acetic acid, although it reacts in the same manner and amount as hydrochloric acid, does not react as quickly. The concepts of strong and weak acids were developed to describe and explain these differences in properties of acids.

An acid is described as *weak* if its characteristic properties are less than those of a common strong acid, such as hydrochloric acid. Weak acids are weaker electrolytes and react at a slower rate than strong acids do; the pH of solutions of weak acids is closer to 7 than the pH of strong acids of equal concentration.

In Chapter 6, strong acids were explained as ionizing quantitatively by reacting with water to form hydronium ions, whereas weak acids were explained as ionizing only partially (usually $<50\%$). The empirical distinction between strong and weak acids can be explained much more completely now by combining the modified Arrhenius theory with equilibrium theory. A strong acid is explained as an acid that reacts quantitatively with water to form hydronium ions. For example, the reaction of dissolved hydrogen chloride (hydrochloric acid) with water is virtually complete. Even though the equation *could* be written with double equilibrium arrows and the extent shown with a $>99.9\%$ note, it is simpler, and much more common, to just use a single arrow to show that the reaction is quantitative.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

A weak acid is an acid that reacts partially with water to form hydronium ions. Measurements of pH indicate that most weak acids react less than 50%. For example, acetic acid reacts only 1.3% in solution at 25 °C and 0.10 mol/L concentration.

Learning Tip

For any aqueous solution of an acid, percent reaction of that acid with water is also commonly called its percent ionization in chemistry references, because the net effect is the same as if the acid molecules simply ionize, as was once (simplistically) assumed in Arrhenius' original theory.

You should consider "reaction with water" and "ionization in water" to be equivalent terms for acid–base solution theory, and may expect to see either term used routinely in text and in questions.

Figure 6
In solutions of equal concentration, a weak acid such as acetic acid conducts electricity to a lesser extent than does a strong acid such as hydrochloric acid.

Recall, from Chapter 15, that any equilibrium position depends on concentration(s) as well as on temperature; so, this 1.3% ionization value for acetic acid is *only* valid for a 0.10 mol/L solution at 25 °C. Laboratory pH experiments show that the higher the concentration of a weak acid solution, the lower its percent ionization becomes.

$$CH_3COOH(aq) + H_2O(l) \overset{1.3\%}{\rightleftarrows} H_3O^+(aq) + CH_3COO^-(aq)$$

The hydronium ion concentration of any acid solution can be calculated by multiplying the percent reaction by the initial amount concentration of the acid solute. For example, in HCl(aq) solution, virtually 100% of the HCl molecules react with water molecules at equilibrium.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

$$[H_3O^+(aq)] = \frac{100}{100} \times 0.10 \text{ mol/L}$$

$$= 0.10 \text{ mol/L}$$

There are six acids ordinarily classed as "strong": hydrochloric, nitric, sulfuric, hydrobromic, hydroiodic, and perchloric acid solutions. Only the first three are common.

For any aqueous strong acid, we can simply assume that the concentration of hydronium ions in solution is equal to the initial concentration of the acid dissolved. For weak acids (the majority of examples), we always need to calculate the hydronium ion concentration in solution, because only a small proportion of the initial acid concentration will be converted to ions at equilibrium.

COMMUNICATION example 5

In a 0.10 mol/L solution of acetic acid, only 1.3% of the CH_3COOH molecules have reacted at equilibrium to form hydronium ions. Calculate the hydronium ion amount concentration.

Solution

$$CH_3COOH(aq) + H_2O(l) \xrightarrow{1.3\%} H_3O^+(aq) + CH_3COO^-(aq)$$

$$[H_3O^+(aq)] = \frac{1.3}{100} \times 0.10 \text{ mol/L}$$

$$= 1.3 \times 10^{-3} \text{ mol/L}$$

The hydronium ion concentration in 0.10 mol/L acetic acid is 1.3×10^{-3} mol/L.

As explained in Chapter 6, we can easily compare the strengths of different acids by comparing the measured pH values for aqueous solutions of equal concentration. The lower the pH, the higher the hydronium ion concentration, the greater the percent reaction, and thus the stronger the acid. Furthermore, we can find the percent reaction for ionization of any weak acid solution from the measured pH of a solution of known initial concentration.

Learning Tip

Percent ionization:

$$p = \frac{[H_3O^+(aq)]}{[HA(aq)]} \times 100$$

Rearrange the equation to solve for the equilibrium hydronium ion concentration:

$$[H_3O^+(aq)] = \frac{p}{100} \times [HA(aq)]$$

where p = percent ionization
and
$[HA(aq)]$ = initial concentration of weak acid

COMMUNICATION example 6

The pH of a 0.10 mol/L methanoic acid solution is 2.38. Calculate the percent reaction for ionization of methanoic acid.

Solution

$$[H_3O^+(aq)] = 10^{-pH}$$

$$= 10^{-2.38} \text{ mol/L}$$

$$= 4.2 \times 10^{-3} \text{ mol/L}$$

$$[H_3O^+(aq)] = \frac{p}{100 \times [HCOOH(aq)]}$$

$$p = \frac{[H_3O^+(aq)]}{[HCOOH(aq)]} \times 100$$

$$= \frac{4.2 \times 10^{-3} \text{ mol/L}}{0.10 \text{ mol/L}} \times 100$$

$$= 4.2\%$$

The percent ionization of 0.10 mol/L aqueous methanoic acid is 4.2%.

WEB Activity

Canadian Achievers—Edgar Steacie

Edgar Steacie (**Figure 7**) was an internationally acclaimed research scientist and a senior administrator of the National Research Council.

1. What was Steacie's main area of research?
2. Why was Steacie known as a statesman of science for Canada?
3. What is a Steacie Fellowship?

www.science.nelson.com GO

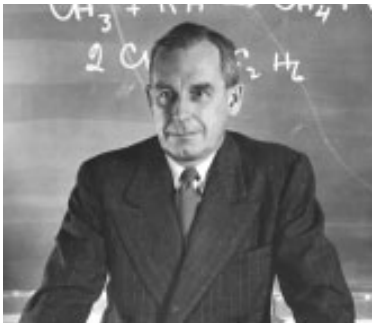


Figure 7
Edgar Steacie (1900–1962)

Section 16.1 Questions

1. How does the hydronium ion concentration compare with the hydroxide ion concentration if a solution is
   (a) neutral?
   (b) acidic?
   (c) basic?
2. What two diagnostic tests can distinguish a weak acid from a strong acid?
3. According to Arrhenius' original theory, what do all bases have in common?
4. Hydrocyanic acid is a very weak acid.
   (a) Write an equilibrium reaction equation for the ionization of 0.10 mol/L HCN(aq). The percent ionization at SATP is 7.8×10^{-3}%.
   (b) Calculate the hydronium ion concentration and the pH of a 0.10 mol/L solution of HCN(aq).
5. At 25 °C, the hydronium ion concentration in vinegar is 1.3 mmol/L. Calculate the hydroxide ion concentration.
6. At 25 °C, the hydroxide ion concentration in normal human blood is 2.5×10^{-7} mol/L. Calculate the hydronium ion concentration and the pH of blood.
7. Acid rain has a pH less than that of normal rain. The presence of dissolved carbon dioxide, which forms carbonic acid, gives normal rain a pH of 5.6. What is the hydronium ion concentration in normal rain?
8. If the pH of a solution changes by 3 pH units as a result of adding a weak acid, by how much does the hydronium ion concentration change?
9. If 8.50 g of sodium hydroxide is dissolved to make 500 mL of cleaning solution, determine the pOH of the solution.
10. What mass of hydrogen chloride gas is required to produce 250 mL of a hydrochloric acid solution with a pH of 1.57?
11. Determine the pH of a 0.10 mol/L hypochlorous acid solution, which has 0.054% ionization at 25 °C.
12. Calculate the pH and pOH of a hydrochloric acid solution prepared by dissolving 30.5 kg of hydrogen chloride gas to make 806 L of solution. What assumption is made when doing this calculation?
13. Acetic (ethanoic) acid is the most common weak acid used in industry. Determine the pH and pOH of an acetic acid solution prepared by dissolving 60.0 kg of pure, liquid acetic acid to make 1.25 kL of solution. The percent reaction with water at this concentration is 0.48%.
14. Determine the mass of sodium hydroxide that must be dissolved to make 2.00 L of a solution with a pH of 10.35.
15. Write an experimental design for the identification of four colourless solutions: a strong acid solution, a weak acid solution, a neutral molecular solution, and a neutral ionic solution. Write sentences, create a flow chart, or design a table to describe the required diagnostic tests.
16. Sketch a flow chart or concept map that summarizes the conversion of $[H_3O^+(aq)]$ to and from $[OH^-(aq)]$, pH, and percent reaction (ionization) of acid solute. Make your flow chart large enough that you can write the procedure between the quantity symbols in the diagram.

16.2 The Brønsted–Lowry Acid–Base Concept

By now, our much-revised acid and base theory includes concepts of hydronium ions, reaction with water, reaction equilibrium, and the ionization equilibrium of water. Our modified theory is, thus, much more comprehensive, and much better at describing, explaining, and predicting acid–base reactions, than the original theory proposed by Arrhenius. We find, however, that there are still problems, and our theory must still be considered too restrictive. There is no provision in it for reactions that do not occur in aqueous solution. In addition, we find that there are some substances that seem to have both acid and base properties.

As a common example, sodium hydrogen carbonate (sodium bicarbonate, baking soda) forms a basic solution (raises the pH) in water, but the same compound will partly neutralize (lower the pH of) a sodium hydroxide (lye) solution. When we observe that $NaHCO_3(s)$ forms a basic aqueous solution, we conclude that this happens because some hydrogen carbonate ions react with water molecules to produce hydroxide ions. We know from many other observations that sodium ions have no acidic or basic properties. The following reaction equation seems to explain our observation easily:

$$HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$$

But, if adding sodium hydrogen carbonate makes a (strongly basic) sodium hydroxide solution less basic, the concepts we are using lead us to conclude that something must be reacting to decrease the concentration of the hydroxide ions. It must be the hydrogen carbonate ions because there are no other entities in this system except sodium ions and water molecules. We can easily write an equation to explain this observation, as well:

$$HCO_3^-(aq) + OH^-(aq) \rightleftarrows CO_3^{2-}(aq) + H_2O(l)$$

This equation seems to explain how the hydroxide ions can be partially consumed. But, if it is correct, it begs the question, "Is sodium bicarbonate a base, or is it an acid?" Clearly, our theory still needs some work! We need a broader, more comprehensive concept to successfully explain these kinds of observations.

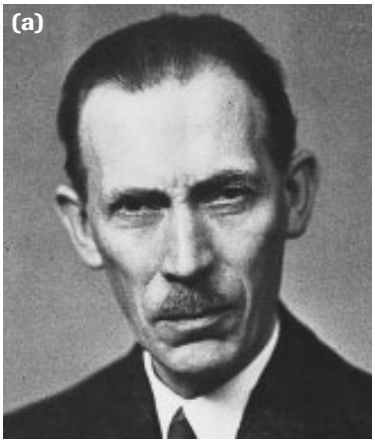


Figure 1
Johannes Brønsted (1879–1947) **(a)** and Thomas Lowry (1874–1936) **(b)** independently created new theoretical definitions for acids and bases, based upon proton transfer during a reaction.

The Proton Transfer Concept

New theories in science usually result from looking at the evidence in a way that has not occurred to other observers. In 1923, two European scientists independently developed a new approach to acids and bases (**Figure 1**). These scientists focused on the role of an acid and a base *in a reaction* rather than on the acidic or basic properties of their aqueous solutions. An acid, such as hydrogen chloride, functions in a way opposite to a base, such as ammonia. According to the Brønsted–Lowry concept, hydrogen chloride, upon dissolving, *donates* a proton to a water molecule:

$$\underset{\text{acid}}{HCl(aq)} + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \quad (H^+ \text{ transferred})$$

and ammonia, upon dissolving, *accepts* a proton from a water molecule.

$$NH_3(aq) + \underset{\text{base}}{H_2O(l)} \rightleftarrows OH^-(aq) + NH_4^+(aq) \quad (H^+ \text{ transferred})$$

Water does not have to be one of the reactants. For example, hydronium ions present in a hydrochloric acid solution can react directly with dissolved ammonia molecules.

$$\underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{NH_3(aq)} \rightarrow H_2O(l) + NH_4^+(aq)$$

(H^+ transfers from H_3O^+ to NH_3)

We can describe this reaction as NH_3 molecules removing protons from H_3O^+ ions. Hydronium ions act as the acid, and ammonia molecules act as the base. Water is present as the solvent but not as a primary reactant. In fact, water does not even have to be present, as evidenced by the reaction of hydrogen chloride and ammonia gases (**Figure 2**).

$$\underset{\text{acid}}{HCl(g)} + \underset{\text{base}}{NH_3(g)} \rightarrow NH_4Cl(s)$$

(H^+ transfers from HCl to NH_3)

Figure 2
Invisible fumes of ammonia gas and hydrogen chloride gas mix and react above these beakers, producing tiny visible particles of solid ammonium chloride that are suspended in the air.

According to the Brønsted–Lowry concept, a **Brønsted–Lowry acid** is a proton donor and a **Brønsted–Lowry base** is a proton acceptor. A Brønsted–Lowry neutralization is a competition for protons that results in a proton transfer from the strongest acid present to the strongest base present. A **Brønsted–Lowry reaction equation** is an equation written to show an acid–base reaction involving the transfer of a proton from one entity (an acid) to another (a base).

The Brønsted–Lowry concept does away with defining a *substance* as being an acid or base. Only an *entity* that is involved in a proton transfer in a reaction can be defined as an acid or base—and only for that particular reaction. This last point is extremely important: protons may be gained in a reaction with one entity, but lost in a reaction with another entity. For example, in the reaction of HCl with water shown on the previous page, water acts as the base; whereas, in its reaction with NH_3, water acts as the acid. A substance that appears to act as a Brønsted–Lowry acid in some reactions and as a Brønsted–Lowry base in other reactions is called amphoteric, or sometimes (incorrectly) amphiprotic. The empirical term, **amphoteric**, properly refers to a chemical *substance* with the ability to react as either an acid or a base. The theoretical term, **amphiprotic**, describes an *entity* (ion or molecule) having the ability to either accept or donate a proton. The hydrogen carbonate ion in baking soda (**Figure 3**), like every other hydrogen polyatomic ion, is amphiprotic, as shown by the following reactions:

Figure 3
Baking soda is a common household chemical, but it requires an uncommonly sophisticated theory to describe, explain, or predict all of its properties.

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftarrows OH^-(aq) + H_2CO_3(aq) \qquad K_c = 2.2 \times 10^{-8}\ \text{mol/L}$$

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftarrows H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_c = 4.7 \times 10^{-11}\ \text{mol/L}$$

When bicarbonate ions are in aqueous solution, some react with the water molecules by acting as an acid, and some react by acting as a base. K_c values given for these two equilibriums show that one of them predominates—so much so that the other reaction is simply inconsequential. The number of ions reacting as a base is over 2000 times more than the number reacting as an acid. As you might expect, the resulting solution is basic.

We can get a clearer idea of the amphoteric nature of baking soda (caused by the amphiprotic nature of the hydrogen carbonate ion) by noting the evidence expressed in the next two equations. Note that bicarbonate ions partly neutralize a strong acid, but they can also partly neutralize a strong base.

$$\underset{\text{base}}{HCO_3^-(aq)} + \underset{\text{acid}}{H_3O^+(aq)} \rightleftarrows H_2CO_3(aq) + H_2O(l) \qquad \text{(raises the pH of a strong acid solution)}$$

$$\underset{\text{acid}}{HCO_3^-(aq)} + \underset{\text{base}}{OH^-(aq)} \rightleftarrows CO_3^{2-}(aq) + H_2O(l) \qquad \text{(lowers the pH of a strong base solution)}$$

DID YOU KNOW ?

Superacids

In aqueous solution, all strong acids are equal in strength, since they all react instantly and completely with water to form the strongest possible acid entity that can exist in water—the hydronium ion. Scientists have long suspected, however, that the well-known strong acids, HCl and H_2SO_4, may not be equal in strength when no water is present and that much stronger acids could exist. Dr. Ronald Gillespie of McMaster University has done extensive research on non-aqueous strong acids. His definition of a superacid—one that is stronger than pure sulfuric acid—is now generally accepted by scientists. Perchloric acid, the only common superacid, easily loses protons to $H_2SO_4(l)$ molecules. Fluorosulfonic acid, $HSO_3F(l)$, is more than one thousand times stronger than $H_2SO_4(l)$. It is the strongest Brønsted–Lowry acid known.

Figure 4
White vinegar is a 5% acetic (ethanoic) acid solution. The amount concentration is 0.83 mol/L. Such a solution is only about 0.43% ionized at 25 °C, making acetic acid a typical weak acid, by definition.

Scientists consider the Brønsted–Lowry concept to be a theoretical definition. It falls short of being a comprehensive theory because it does not explain *why* a proton is donated or accepted, and cannot predict theoretically *which* reaction will occur for a given entity in any given new situation. *The advantage of the Brønsted–Lowry definitions is that they enable us to define acids and bases in terms of chemical reactions rather than simply as substances that form acidic and basic aqueous solutions.* A definition of acids and bases in terms of chemical reactions allows us to describe, explain, and predict a great many more reactions, whether they take place in aqueous solution, in solution in some other solvent, or between two undissolved entities in pure chemical states.

Practice

1. Theories in science develop over a period of time. Illustrate this development by writing a theoretical definition of an acid, using the following concepts. Begin your answer with, "According to [authority], acids are substances that…."
   (a) Arrhenius' original theory
   (b) the modified Arrhenius theory
   (c) the Brønsted–Lowry concept
2. How does the definition of a base according to the modified Arrhenius theory compare with the Brønsted–Lowry definition?
3. Classify each reactant in the following equations as a Brønsted–Lowry acid or base.
   (a) $HF(aq) + SO_3^{2-}(aq) \rightleftarrows F^-(aq) + HSO_3^-(aq)$
   (b) $CO_3^{2-}(aq) + CH_3COOH(aq) \rightleftarrows CH_3COO^-(aq) + HCO_3^-(aq)$
   (c) $H_3PO_4(aq) + OCl^-(aq) \rightleftarrows H_2PO^{4-}(aq) + HOCl(aq)$
   (d) $HCO_3^-(aq) + HSO_4^-(aq) \rightleftarrows SO_4^{2-}(aq) + H_2CO_3(aq)$
4. Evidence indicates that the hydrogen sulfite ion is amphiprotic. A sodium hydrogen sulfite solution can partly neutralize either a sodium hydroxide spill or a hydrochloric acid spill.
   (a) Write a net ionic equation for the reaction of aqueous hydrogen sulfite ions with the hydroxide ions in solution. Label the reactants as acids or bases.
   (b) Write a net ionic equation for the reaction of hydrogen sulfite ions with the hydronium ions from a hydrochloric acid solution. Label the reactants as acids or bases.
5. What restrictions to acid–base reactions do the Brønsted–Lowry definitions remove?
6. Why is the Brønsted–Lowry concept labelled a theoretical definition rather than a theory?

Conjugate Acids and Bases

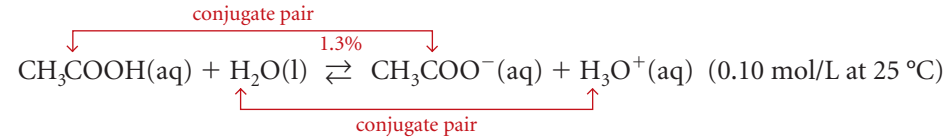
According to the Brønsted–Lowry concept, acid–base reactions involve the transfer of a proton. These reactions are universally reversible and always result in an acid–base equilibrium.

In a proton transfer reaction at equilibrium, both forward and reverse reactions involve Brønsted-Lowry acids and bases. For example, in an acetic acid solution (**Figure 4**), the forward reaction is explained as a proton transfer from acetic acid to water molecules, and the reverse reaction is a proton transfer from hydronium to acetate ions.

$$\underset{\text{acid}}{CH_3COOH(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftarrows \underset{\text{base}}{CH_3COO^-(aq)} + \underset{\text{acid}}{H_3O^+(aq)}$$

(H^+ transferred from CH_3COOH to H_2O; H^+ transferred from H_3O^+ to CH_3COO^-)

This equilibrium is typical of all acid–base reactions. There will always be two acids (in the example, CH_3COOH and H_3O^+) and two bases (in the example, H_2O and CH_3COO^-) in any acid–base reaction equilibrium. Furthermore, the base on the right (CH_3COO^-) is formed by removal of a proton from the acid on the left (CH_3COOH). The acid on the right (H_3O^+) is formed by the addition of a proton to the base on the left (H_2O). A pair of substances with formulas that differ only by a proton is called a **conjugate acid–base pair**. An acetic acid molecule and an acetate ion are a conjugate acid–base pair. Acetic acid is the conjugate acid of the acetate ion, and the acetate ion is the conjugate base of acetic acid. The equation shows that there must always be two conjugate acid–base pairs in any proton transfer reaction. The hydronium ion and water are the second conjugate acid–base pair in this equilibrium. Conjugate acid–base pairs appear opposite each other in a table of acids and bases, such as that in Appendix I.



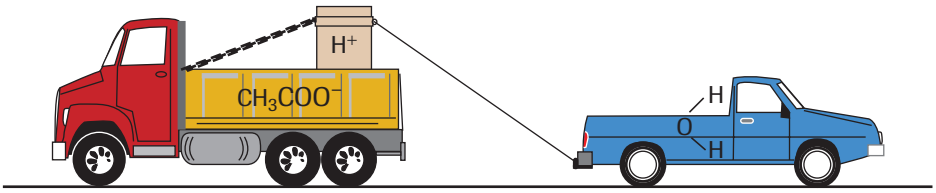


Figure 5
This pictorial analogy is used to explain why acetic acid is a weak acid in aqueous solution. We believe that the proton (H^+) of the carboxyl group is attracted more strongly by the rest of the acetic acid molecule than it is by the water molecule. We infer this conclusion because, at equilibrium, pH evidence indicates that very few of the acetic acid molecules have lost protons in their collisions with water molecules.

At equilibrium, only 1.3% of the CH_3COOH molecules have reacted with water in a 0.10 mol/L solution at SATP. It appears that the ability of the CH_3COO^- part of the acetic acid molecule to keep its proton (H^+) is much greater than the ability of H_2O to attract the proton away (**Figure 5**). This means that CH_3COO^- is a stronger base (it has a greater attraction for protons) than H_2O.

When HCl molecules react with water (**Figure 6**), the Cl^- of each HCl molecule has a much weaker attraction for its proton (H^+) than any colliding water molecule has. The water molecules "win" this "competition" for protons overwhelmingly. At equilibrium, essentially all of the HCl molecules have lost protons to water molecules. In this case, the transfer of protons is quantitative, and, because its molecules have an extremely weak attraction for their protons, HCl(aq) is called (somewhat confusingly) a strong acid.

Remember: The stronger the base, the more it attracts another proton. The stronger an acid, the less it attracts its own proton.

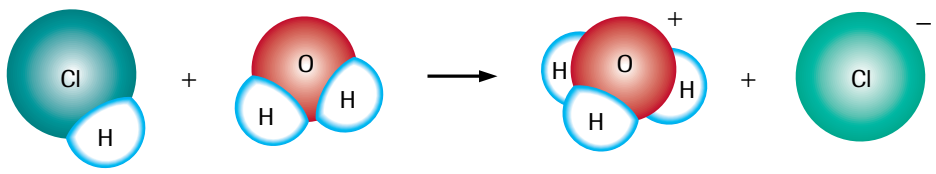


Figure 6
When gaseous hydrogen chloride dissolves in water, the HCl molecules are thought to collide and react quantitatively with water molecules to form hydronium and chloride ions.

Learning Tip

Acids were studied much earlier than bases were, and sometimes the old terminology used to describe acid–base situations can be misleading—because it always focuses on the nature of the acid. Strong acids are very reactive, but we believe it is because they are very weak proton attractors. It is common to speak of acids "donating" protons, and of bases "accepting" them, but this terminology gives an unrealistic view of what we believe is really happening. It is like saying that a bank robber "accepts" money "donated" by a bank teller. The tug-of-war analogy in Figure 5 is a more realistic way to think of proton transfer reactions—as a competition between two bases, both attracting the same proton.

The terms *strong* acid and *weak* acid can be explained in terms of the Brønsted–Lowry concept, and also by comparing the reactions of different acids with the same base—for example, water. Using HA as the general symbol for any acid and A^- as its conjugate base, the empirically derived Relative Strengths of Aqueous Acids and Bases table (Appendix I) lists the position of equilibrium of aqueous solutions of many different acids. They are ordered according to how much they ionize in (react with) the water solvent.

$$HA(aq) + H_2O(1) \rightleftarrows H_3O^+(aq) + A^-(aq)$$

The extent of the proton transfer between HA and H_2O determines the relative strength of HA(aq). In Brønsted–Lowry terms, when a strong acid reacts with water, an almost complete transfer of protons results for the forward reaction and almost no transfer of protons occurs for the reverse reaction; a nearly 100% reaction with water. The equilibrium constant value is found to be very large. Theoretically, a strong acid holds its proton very weakly, and easily loses the proton to any base, even very weak bases such as water. This result leads to the interpretation that the conjugate base, A^-, of a strong acid must have a very weak (negligible) attraction for protons. A useful generalization regarding the relative strengths of an acid–base conjugate pair is: *the stronger an acid, the weaker its conjugate base; and conversely, the weaker an acid, the stronger its conjugate base.* (See the Relative Strengths of Aqueous Acids and Bases table in Appendix I.)

Chemists have no simple explanation, in terms of forces or bonds, for the differing abilities of acids to donate protons or of bases to accept them. The inability to predict acid and base strengths for an entity not already included in an empirically determined table of acids and bases is a major deficiency of all acid–base theories.

SUMMARY Brønsted–Lowry Definitions

- An acid is a proton donor and a base is a proton acceptor, in a specific reaction.
- An acid–base reaction involves a single proton transfer from one entity (the acid) to another (the base).
- An amphiprotic entity (amphoteric substance) is one that acts as a Brønsted–Lowry acid in some reactions and as a Brønsted–Lowry base in other reactions.
- A conjugate acid–base pair consists of two entities with formulas that differ only by a proton.
- A strong acid has a very weak attraction for protons. A strong base has a very strong attraction for protons.
- The stronger an acid, the more weakly it holds its proton. The stronger a base, the more it attracts another proton.
- The stronger an acid, the weaker is its conjugate base. The stronger a base, the weaker is its conjugate acid.

Practice

7. Use the Brønsted–Lowry definitions to identify the two conjugate acid–base pairs in each of the following acid–base reactions.

(a) $HCO_3^-(aq) + S^{2-}(aq) \rightleftarrows HS^-(aq) + CO_3^{2-}(aq)$

(b) $H_2CO_3(aq) + OH^-(aq) \rightleftarrows HCO_3^-(aq) + H_2O(l)$

(c) $HSO_4^-(aq) + HPO_4^{2-}(aq) \rightleftarrows H_2PO_4^-(aq) + SO_4^{2-}(aq)$

(d) $H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$

8. Some ions can form more than one conjugate acid–base pair. List the two conjugate acid–base pairs involving a hydrogen carbonate ion in the reactions in question 7.

INVESTIGATION 16.1 *Introduction*

Creating an Acid–Base Strength Table

An acid–base table organizes common acids (and their conjugate bases) in order of decreasing acid strength. Acid strength can be tested several ways, including by a carefully designed use of indicators. Predict the order of strengths using the Relative Strengths of Aqueous Acids and Bases table (Appendix I). Use the indicators provided to create a valid and efficient Design, in which you clearly identify the relevant variables. Evaluate the Design (only), and suggest improvements if any problems are identified.

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	○ Materials	● Evaluation (1)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

Purpose

The purpose of this investigation is to test an experimental design for using indicators to create a table of relative strengths of acids and bases.

Problem

Can the indicators available be used to rank the acids and bases provided in order of strength?

To perform this investigation, turn to page 768.

Predicting Acid–Base Reaction Equilibria

The Brønsted–Lowry concept unfortunately does not include any theoretical explanation about why any given entity attracts a proton more or less strongly. To predict the outcome of any acid–base combination, we must rely on empirical evidence, gained by measuring and recording the relative strengths of acid and base entities. Predictions must be restricted to only those acid–base combinations for which we already have data. To help us, we can now look for a simple generalization that might allow us to predict the approximate position of equilibrium in an acid–base proton transfer.

LAB EXERCISE 16.B

Predicting Acid–Base Equilibria

Is it possible to predict how far a reaction will proceed? Use the table of Relative Strengths of Aqueous Acids and Bases in Appendix I and the evidence of position of equilibrium to complete the Analysis of the investigation report.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	○ Evaluation
○ Hypothesis	○ Procedure	
○ Prediction	○ Evidence	

Purpose

The purpose of this investigation is to develop a generalization for predicting the position of acid–base equilibria.

Problem

How do the positions of the reactant acid and base in the acid–base table relate to the position of equilibrium?

1. $CH_3COOH(aq) + H_2O(l) \overset{<50\%}{\rightleftarrows} H_3O^+(aq) + CH_3COO^-(aq)$
2. $HCl(aq) + H_2O(l) \overset{>99\%}{\rightleftarrows} H_3O^+(aq) + Cl^-(aq)$
3. $CH_3COO^-(aq) + H_2O(l) \overset{<50\%}{\rightleftarrows} CH_3COOH(aq) + OH^-(aq)$
4. $H_3PO_4(aq) + NH_3(aq) \overset{>50\%}{\rightleftarrows} H_2PO_4^-(aq) + NH_4^+(aq)$
5. $HCO_3^-(aq) + SO_3^{2-}(aq) \overset{<50\%}{\rightleftarrows} HSO_3^-(aq) + CO_3^{2-}(aq)$
6. $H_3O^+(aq) + OH^-(aq) \rightarrow H_2O(l) + H_2O(l)$

WEB Activity

Web Quest—Pool Chemistry

A swimming pool can be an enjoyable place to spend a hot summer afternoon. Most of us are familiar with the dangers of pools. This Web Quest introduces an unfamiliar risk: pool gas. What is it and how does it form? What are the dangers of pool gas, and how can they be reduced?

www.science.nelson.com GO

CAREER CONNECTION

Chemistry Researcher

Farideh Jalilehvand (**Figure 7**) is an associate professor of chemistry at the University of Calgary. Her research involves a lot of X-ray absorption spectroscopy. Find out how acidity due to sulfur accumulation in water-logged wood is connected to ancient shipwrecks by visiting her information site, and check out her curriculum vitae (CV). Science is international in scope!

Figure 7
Farideh Jalilehvand

www.science.nelson.com GO

Predicting Acid–Base Reactions

When making complex predictions, scientists often combine a variety of empirical and theoretical concepts. We need to use a combination of concepts to predict *both* the products and the extent of acid–base reactions. According to the collision–reaction theory, a proton transfer may result from a collision between an acid and a base. In a system that is a mixture of several different acid and/or base entities, there are countless random collisions of all the entities present. So, in theory, in any such system, there are many different possible acid–base reactions, and all of these reactions occur (to some extent) all the time. Evidence indicates that one reaction predominates: it occurs to an extent so much greater than the other reactions that it is the only observable reaction. We will be able to explain which reaction will predominate if we use a combination of the collision–reaction theory and the Brønsted–Lowry concept.

According to collision–reaction theory, in an acid–base system, collisions of all entities present are constantly occurring. According to the Brønsted–Lowry concept, a proton will only transfer if an acid entity collides with a base entity that is a better proton attractor than itself. A proton could theoretically transfer several times (if there were several different acids and bases in the system), transferring each time to a stronger proton attractor. Once gained by an entity of the strongest base present, a proton will remain there, because there is no other base present in the system that can attract that proton strongly enough to remove it. By the same logic, once any entity of the strongest acid present has lost its proton, its (remaining) conjugate base cannot gain one back from any other entity present, because it is a weaker proton attractor than anything else in the system. Overall, theory suggests that the predominant acid–base reaction should be the one that involves proton transfer from the strongest acid to the strongest base present in the system. Experimental evidence indicates that this explanation is correct. Other possible proton transfer reactions occur to such a small extent that they have a negligible effect on the reactants and products, so they are normally ignored.

We theorize that the only significant reaction in any acid–base system involves proton transfer from the strongest acid present to the strongest base present. For an aqueous solution system, we first must list all the entities present *as they exist in aqueous solution*. **Table 1** summarizes how to represent the entities that are present.

Table 1 Predominant Entities Present in Aqueous Solution (other than $H_2O(l)$)

Substance dissolved (example)	Kinds of entities in solution	Predominant entities present (example)
Ionic compounds $Ca(HCO_3)_2(aq)$	cations, anions	$Ca^{2+}(aq)$ and $HCO_3^-(aq)$
Ionic oxides $Na_2O(aq)$, $CaO(aq)$	cations, hydroxide ions	$Na^+(aq)$, $OH^-(aq)$ or $Ca^{2+}(aq)$, $OH^-(aq)$
Strong acids $HCl(aq)$ or $HNO_3(aq)$	$H_3O^+(aq)$, conjugate base	$H_3O^+(aq)$, $Cl^-(aq)$ or $H_3O^+(aq)$, $NO_3^-(aq)$
Weak acids $HF(aq)$ or $HSO_3^-(aq)$	molecules or ions	$HF(aq)$ or $HSO_3^-(aq)$
Weak bases $NH_3(aq)$ or $HCO_3^-(aq)$	molecules or ions	$NH_3(aq)$ or $HCO_3^-(aq)$

The process for determining the nature and extent of the predominant proton transfer reaction in an aqueous acid–base system can be thought of as five distinct steps, for convenience, as shown in the following Sample Problem.

SAMPLE problem 16.1

What will be the predominant reaction if spilled drain cleaner (sodium hydroxide) solution is neutralized with vinegar (**Figure 8**)? Are reactants or products favoured in this reaction?

Step 1: List all entities present as they exist in aqueous solution. Refer to **Table 1** if necessary. The entity list for this situation is

$Na^+(aq)$ $OH^-(aq)$ $CH_3COOH(aq)$ $H_2O(l)$

Step 2: Use the entity lists of the Relative Strengths of Aqueous Acids and Bases table to identify and label each entity present as a Brønsted–Lowry acid or base. Amphiprotic entities are labelled for *both* possibilities. Conjugate bases of strong acids are *not* included or labelled as bases because they cannot *act* as bases in aqueous solution. Metal ions are treated as spectators.

$Na^+(aq)$	$OH^-(aq)$	$CH_3COOH(aq)$	$H_2O(l)$
	B	**A**	**A**, **B**

Step 3: Use the *order* of the entities in the Relative Strengths of Aqueous Acids and Bases table to identify and label the *strongest* Brønsted–Lowry acid (the highest one on the table) and the *strongest* Brønsted–Lowry base (the lowest one on the table) that are present in the solution.

$Na^+(aq)$	$OH^-(aq)$	$CH_3COOH(aq)$	$H_2O(l)$
	SB	**SA**	**A**, **B**

Step 4: Write a balanced equation to show a proton transfer from the strongest acid to the strongest base, assuming that their respective conjugates are the reaction products.

$$CH_3COOH(aq) + OH^-(aq) \rightleftarrows CH_3COO^-(aq) + H_2O(l)$$

(H^+ transferred from CH_3COOH to OH^-)

Step 5: Predict the position of equilibrium using the generalization developed in Lab Exercise 16.B and illustrated in the margin Learning Tip. For this reaction, the strongest acid is positioned higher on the table than the strongest base, so products are favoured. *Under certain assumed conditions* (see the following discussion), the equilibrium percent reaction may be labelled as greater than 50%.

$$CH_3COOH(aq) + OH^-(aq) \overset{>50\%}{\rightleftarrows} CH_3COO^-(aq) + H_2O(l)$$

Figure 8
The drain cleaner shown is a concentrated solution of a very strong base. A spill would be highly corrosive and quite hazardous. Excess weak acid, such as the vinegar (5% acetic acid), is the best choice to "neutralize" a spilled strong base. The final solution will not actually be neutral, but it will be only mildly acidic, and much safer to handle.

The nature of water complicates the prediction of outcomes of acid–base reactions in aqueous solution. We need to consider the specific restrictions that apply when predicting proton transfer reactions *in aqueous solution*, because they are much more common than acid–base reactions in any other environment.

- Hydronium ion is the strongest acid entity that can exist in aqueous solution. If a stronger acid than hydronium ion is dissolved in water, it reacts instantly and completely with water molecules to form hydronium ions. For this reason, the six strong acids are all written as $H_3O^+(aq)$ when in aqueous solution.
- Hydroxide ion is the strongest base entity that can exist in aqueous solution. If a stronger base than hydroxide ion is dissolved in water, it reacts instantly and completely to form hydroxide ions. The only common example is the dissolving of soluble ionic oxide compounds such as $Na_2O(s)$. In such cases, the oxide ion is written as $OH^-(aq)$ when in aqueous solution.

Learning Tip

The relative positions of the strongest acid and the strongest base on an acid–base table can be used to approximately determine the position of an acid–base equilibrium.

Products Favoured

SA + **SB** $\overset{>50\%}{\rightleftarrows}$

Reactants Favoured

SB + **SA** $\overset{<50\%}{\rightleftarrows}$

Learning Tip

Since hydroxide ion is the strongest possible base in aqueous solution, reaction of any acid with this ion in aqueous solution is automatically one that favours products. Similarly, the reaction of any base with the strongest possible acid, hydronium ion, must favour products. Of course, the reaction of hydroxide ion with hydronium ion is always quantitative.

- No entity in aqueous solution can react as a base if it is a weaker base than water. For this reason, the conjugate bases of the six strong acids are not considered as bases, in aqueous solution.

Even though you find that products are favoured (as in Sample Problem 16.1), for the predominant reaction, you cannot accurately predict the actual equilibrium position of all cases of any specific acid–base reaction by this method. It simply means you know that the forward reaction happens more readily than the reverse reaction, all things being equal. But, recall (from Chapter 15) that the initial concentration of entities plays a very large part in determining the percent reaction at equilibrium. To be able to predict something meaningful about the position of an acid–base reaction equilibrium, we must restrict the reaction conditions. Unless you are specifically informed otherwise in a question, assume in this text that, for the predominant reaction in an acid–base system,

- the equation represents a single proton transfer between two entities, neither of which is water, and has a stoichiometric ratio of 1:1:1:1
- the strongest acid and the strongest base present in the reaction system are both present in significant chemical amounts, in approximately equal concentrations

Under these circumstances (and only then), you may assume that a Brønsted–Lowry acid–base reaction where products are favoured has a percent reaction greater than 50%, or that a reaction where reactants are favoured may be labelled as "$<$ 50%." It is also correct (given these restrictions) to state that the K_c value for any such reaction is > 1 if products are favoured, and < 1 if reactants are favoured. It is not possible to be more precise about the equilibrium position, however, at our current level of theory.

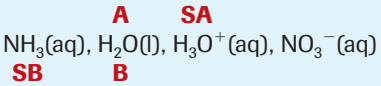
Note that the above restrictions exclude any reaction equation written to describe the ionization (reaction with water) of any single acid or base entity dissolved to make an aqueous solution. In these cases, water is acting as one of the reactants, and the amount concentration of the water is very much greater than that of the other entity.

Finally, recall that the reaction of hydronium ions with hydroxide ions is always quantitative. This equation should always be written with a single arrow. There are many other acid–base reactions that are quantitative, particularly those where either hydronium or hydroxide ions are involved, but it is not possible to easily predict whether any acid–base reaction will be quantitative from the table of Relative Strengths of Aqueous Acids and Bases. In this text, *other quantitative reactions will always be identified for you*, as in the following Communication Example.

COMMUNICATION example

Ammonium nitrate fertilizer is produced by the quantitative reaction of aqueous ammonia with nitric acid. Write a balanced acid–base equilibrium equation.

Solution



$$NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)$$

SUMMARY A Five-Step Method for Predicting the Predominant Acid–Base Reaction

1. List all entities (ions, atoms, or molecules including $H_2O(l)$) initially present as they exist in aqueous solution. (Refer to Table 1, page 728.)
2. Identify and label all possible aqueous acids and bases, using the Brønsted–Lowry definitions.
3. Identify the strongest acid and the strongest base present, using the table of Relative Strengths of Aqueous Acids and Bases (Appendix I).
4. Write an equation showing a transfer of one proton from the strongest acid to the strongest base, and predict the conjugate base and the conjugate acid to be the products.
5. Predict the approximate position of the equilibrium, using the generalization developed in Lab Exercise 16.B on page 727, the Learning Tip on page 729, and the table of Relative Strengths of Aqueous Acids and Bases (Appendix I).

Practice

Use the five-step method to predict the predominant reactions in the following chemical systems:

9. Hydrofluoric acid and an aqueous solution of sodium sulfate are mixed to test the five-step method of predicting acid–base reactions.

10. Strong acids, such as perchloric acid, have been shown to react quantitatively with strong bases, such as sodium hydroxide.

11. Methanoic acid is added to an aqueous solution of sodium hydrogen sulfide.

12. A student mixes solutions of ammonium chloride and sodium nitrite in a chemistry laboratory.

13. Empirical work has shown that nitric acid reacts quantitatively with a sodium acetate solution.

14. A consumer attempts to neutralize an aqueous sodium hydrogen sulfate cleaner with a solution of lye. (See Appendix J if you do not remember what lye is.)

15. Can ammonium nitrate fertilizer, added to water, be used to neutralize a muriatic acid (hydrochloric acid) spill?

16. Predict the acid–base reaction of bleach with vinegar (**Figure 9**).

17. Commercial laundry bleach (Figure 9) is made by reacting chlorine gas with a sodium hydroxide solution, according to the equation

$$Cl_2(g) + 2\,OH^-(aq) \rightleftarrows OCl^-(aq) + Cl^-(aq) + H_2O(l)$$

As sold, the pH of laundry bleach solutions is always well above 8. You know that the element chlorine has very low solubility in pure water. Explain, using Le Châtelier's principle, why bleach bottle labels warn so strongly against mixing bleach with other cleaning agents, such as acidic toilet bowl cleaners.

Note: Household bleach also produces toxic chloramines if mixed with basic ammonia cleaning solutions. The best rule is, NEVER mix bleach directly with any other cleaning powder or solution. It is arguably the most dangerous common household chemical.

CAUTION: Do not mix
with a toilet bowl clean-
er, rust remover, house-
hold ammonia or acids.
Never directly mix con-
JAVEX can save you money by replacing
many expensive household products. It's
an effective cleaner, deodorizer and
disinfectant all rolled into one. For infor-
mation on the many uses of JAVEX, see
the yellow box below. One example is:
Dishes and Pots: The easy, economical way to clean
and remove stains without scratching porcelain fin-
ish. Wipe with solution of 60 mL (¼ cup) JAVEX in
1 litre water. Let stand a few minutes before rinsing.
JAVEX WILL NOT DISINFECT OR WHITEN LAUNDRY.
How to use JAVEX with your detergent in
the laundry.
Directions:
1. Add 250 mL of JAVEX with your detergent.
2. Pour JAVEX into wash water before adding
laundry. Or dilute JAVEX in 1 litre of water and
add after agitation starts.
3. Pre-soak stubborn stains for 5 minutes in a
solution of 125 mL of JAVEX to 5 litres water.
Wash normally with JAVEX and detergent.

Figure 9
Bottles of household bleach display a warning against mixing the bleach (aqueous sodium hypochlorite) with acids. Does your prediction of the reaction between vinegar and hypochlorite ions provide any clues about the reason for the warning?

LAB EXERCISE 16.C

Aqueous Bicarbonate Ion Acid–Base Reactions

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ● Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ○ Evidence
- ● Analysis
- ● Evaluation (2, 3)

An acid–base table organizes common acids (and their conjugate bases) in a way that enables us to predict predominant acid–base reactions. Evaluate the reliability of the five-step method (only) using information from this investigation, by comparing your analysis of the evidence with your predictions.

Purpose

The purpose of this investigation is to test the five-step method for predicting reactions in acid–base systems.

Problem

What are the products and position of the equilibrium for sodium hydrogen carbonate (**Figure 10**) with stomach acid, vinegar, household ammonia, and lye, respectively?

Evidence

Table 2 The Addition of Baking Soda to Various Solutions

Reactant	Bubbles	Odour	pH
HCl(aq)	yes	none	increases
$CH_3COOH(aq)$	yes	disappears	increases
$NH_3(aq)$	no	remains	decreases
NaOH(aq)	no	none	decreases

Figure 10
The versatility of baking soda is demonstrated by its use in extinguishing fires, in baking biscuits, and in neutralizing excess stomach acid. It is also used as a medium for local anesthetics—baking soda reduces stinging sensations by neutralizing the acidity of the anesthetic, with the result that the speed and efficiency of the anesthetic are improved. The broad range of uses for baking soda results, in part, from its amphiprotic character.

INVESTIGATION 16.2 *Introduction*

Testing Brønsted–Lowry Reaction Predictions

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ● Prediction
- ○ Design
- ● Materials
- ● Procedure
- ● Evidence
- ● Analysis
- ● Evaluation (1, 2, 3)

When predicting products for this investigation, list all entities present as they normally exist in an aqueous environment. For those reactants that are added in solid state, assume that they will dissolve. Use the resulting entities for prediction. Evaluate the predictions, the Brønsted–Lowry concept, and the five-step method for acid–base reaction prediction.

Purpose

The purpose of this investigation is to test the Brønsted–Lowry concept and the five-step method for reaction prediction from a table of relative acid–base strength.

Problem

What reactions occur when various pairs of substances are mixed?

Design

A prediction is made for each of eleven pairs of substances. The prediction is then tested using one or more diagnostic tests, complete with controls. Additional diagnostic tests increase the certainty of the evaluation.

To perform this investigation, turn to page 768.

LAB EXERCISE 16.D

Creating an Acid–Base Table

Complete the Analysis of the investigation report, including a short table of the four acids and bases involved. Use entity position generalizations in the acid–base table for reactions that favour products or reactants. The evidence for reaction 1 is interpreted as:

Acids **Bases**

$CH_3COOH(aq)$ ——(>50%)—— $C_3H_7COO^-(aq)$

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ○ Evidence
- ● Analysis
- ○ Evaluation

Purpose

The purpose of this investigation is to test an experimental design for using equilibrium position to create a table of relative strengths of acids and bases.

Problem

What is the order of acid strength for the first four members of the carboxylic acid family?

Evidence

$$CH_3COOH(aq) + C_3H_7COO^-(aq) \overset{>50\%}{\rightleftarrows} CH_3COO^-(aq) + C_3H_7COOH(aq)$$

$$HCOOH(aq) + CH_3COO^-(aq) \overset{>50\%}{\rightleftarrows} HCOO^-(aq) + CH_3COOH(aq)$$

$$C_2H_5COOH(aq) + C_3H_7COO^-(aq) \overset{<50\%}{\rightleftarrows} C_2H_5COO^-(aq) + C_3H_7COOH(aq)$$

$$C_2H_5COOH(aq) + HCOO^-(aq) \overset{<50\%}{\rightleftarrows} C_2H_5COO^-(aq) + HCOOH(aq)$$

Case Study

Changing Ideas on Acids and Bases—The Evolution of a Scientific Theory

Historically, chemists have known the empirical properties of substances long before any theory was developed to explain and predict those properties. For example, chemists were familiar with the distinguishing properties of several acids and bases, and used them routinely, by the middle of the 17th century. Early attempts at an acid–base theory tended to focus on acids and to ignore bases. Over time, several theories passed through cycles of formulation, testing, acceptance, further testing, and eventual rejection. Following is a brief historical summary of acid–base theories and the evidence that led to their revision.

- **Antoine Lavoisier** (1743–1794) (**Figure 11**) believed that the properties of acids could be traced back to a single substance. Lavoisier studied the combustion of phosphorus and sulfur and determined that these elements combine with something in the atmosphere to produce compounds that form acidic solutions when dissolved in water. When Joseph Priestley identified the component of the atmosphere that actively supports combustion, Lavoisier (1777) named the gas *oxygen*, meaning "acid maker." Lavoisier assumed that oxygen was the substance responsible for the generic properties of acids. There were soon problems with this theory when it was found that several acids, such as muriatic acid (HCl), do not contain oxygen. Furthermore, many substances that form basic solutions (such as lime, CaO) *were* found to contain oxygen. This evidence led to the rejection of the oxygen theory, but it is historically important because it is the first systematic attempt to chemically characterize acids and bases. The generalization that nonmetallic oxides form acidic solutions is still useful in chemistry.
- **Sir Humphry Davy** (1778–1829) (**Figure 12**) conducted the experiments that demonstrated the absence of oxygen in muriatic acid (HCl), which led to the rejection of Lavoisier's theory. Davy (1810) advanced his own theory that the

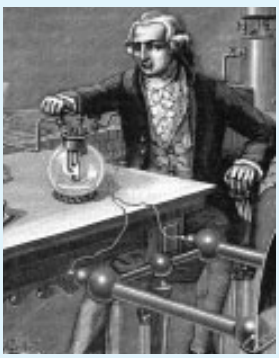


Figure 11
Antoine Lavoisier

Figure 12
Humphry Davy

presence of hydrogen gives compounds acidic properties. This theory, however, did not explain why many compounds containing hydrogen have neutral properties (for example, CH_4) or basic properties (for example, NH_3). Justus von Liebig (1803–1873) revised Davy's idea to define acids as substances in which the hydrogen could be replaced by a metal. This revision meant that acids could be thought of as ionic compounds in which hydrogen had replaced the metal ion. Liebig had no corresponding theoretical definition for bases, which were still identified empirically as substances that neutralized acids.

- **Svante Arrhenius** (1859–1927) (**Figure 13**) developed a theory in 1887 that provided the first useful theoretical definitions of acids and bases. He defined acids as *substances that ionize in aqueous solution to form hydrogen ions*, $H^+(aq)$. Similarly, he defined bases as *substances that dissociate to form hydroxide ions*, $OH^-(aq)$, *in solution.* This theory explained the process of neutralization as the combination of hydrogen ions and hydroxide ions to form water

Figure 13
Svante Arrhenius

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Arrhenius explained the strengths of acids in terms of degrees of ionization. While these ideas were a major development in chemists' understanding of the properties of acids and bases, there were some problems with Arrhenius' theory.

  - In Arrhenius' theory, an acid is expected to be an acid in any solvent, which was found not to be the case. For example, when dissolved in water, HCl supposedly breaks up into hydrogen ions and chloride ions, but when it is dissolved in benzene, the HCl remains as intact molecules. The nature of the solvent, therefore, had to play a critical role in acid–base properties of substances.
  - The need for hydroxide to always be the base led Arrhenius to propose formulas such as $NH_4OH(aq)$ for the formula for ammonia in water, which led to the misconception that $NH_4OH(aq)$ was the base, not $NH_3(aq)$.
  - According to Arrhenius' theory, all salts (ionic solids) should produce neutral solutions, but many do not. For example, solutions of ammonium chloride are acidic and solutions of sodium acetate are basic.
  - Bonding theory suggested that it was very unlikely that a single proton could exist in aqueous solution without being bonded to at least one water molecule.

- **Johannes Brønsted** (1879–1947) (**Figure 14**) and **Thomas Lowry** (1874–1936) (**Figure 15**) independently published (1923) essentially the same concept about how acids and bases behave. These scientists focused on the role of an acid and a base in a reaction rather than on the properties of their aqueous solutions. According to the Brønsted–Lowry concept, *an acid is a proton (H^+) donor* and *a base is a proton acceptor*. The solvent has a central role in the Brønsted–Lowry concept. Water can be considered an acid or a base since it can lose a proton to form a hydroxide ion (OH^-) or accept a proton to form a hydronium ion (H_3O^+). In their view, neutralization is a competition for protons that results in a proton transfer from the strongest acid present to the strongest base present. For example, in the reaction

Figure 14
Johannes Brønsted

Figure 15
Thomas Lowry

$$HSO_4^-(aq) + NH_3(aq) \rightarrow SO_4^{2-}(aq) + NH_4^+(aq)$$

the hydrogen sulfate ion acts as the acid (because it donates a proton) and ammonia acts as the base (because it accepts a proton). A weakness of the Brønsted–Lowry concept is its limitation to solutions (gaseous or liquid).

- **Gilbert Lewis** (1875–1946) (**Figure 16**) developed an acid–base theory in 1923 that includes all previous theories and definitions of acids and bases. He viewed acids and bases in terms of the covalent bond, a theory he had developed in 1916. Lewis defined acids as *electron–pair acceptors* and bases as *electron–pair donors*. It is important to note that in Lewis acid–base theory, no hydrogen ion and no solvent need be involved. The Lewis definition is broader than all previous definitions and explains more inorganic and organic reactions (**Figure 17**). For example, in the reaction

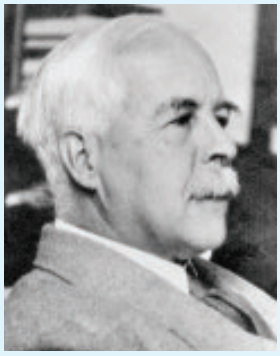


Figure 16
Gilbert Lewis

$$BF_3(g) + NH_3(g) \rightarrow H_3NBF_3(g)$$

boron trifluoride acts as a Lewis acid because it accepts (forms a bond with) a pair of electrons from the ammonia, which acts as the Lewis base.

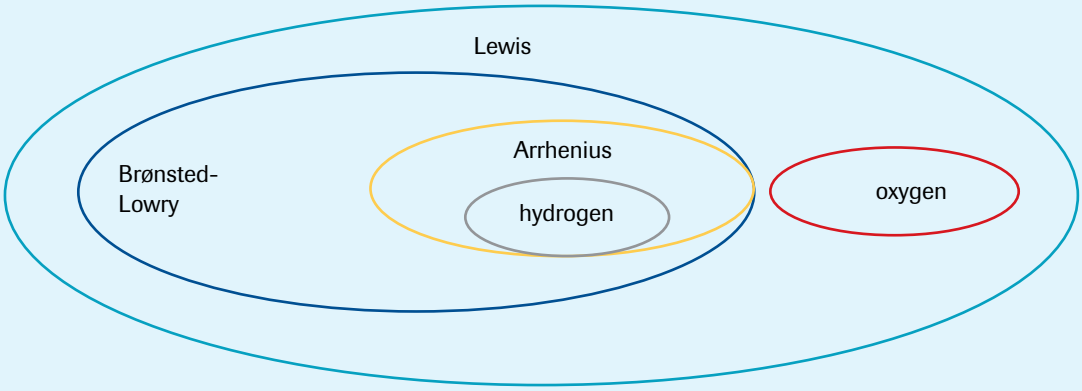


Figure 17
This Venn diagram shows how comprehensive some different acid–base theories are considered to be.

In science, it is unwise to assume that any scientific concept is complete. Whenever scientists assume that they understand a concept, two things usually happen. First, conceptual knowledge tends to remain static for a while because little conflicting evidence exists, or because conflicting evidence (being somewhat discomfiting) is ignored. Second, when enough conflicting evidence accumulates, a change in thinking occurs within the scientific community in which the current theory is drastically revised or entirely replaced. Revolutionary concepts most often tend to be formed in a moment of insight, usually following a long period of incredibly hard work done by a great many people.

Case Study Questions

1. Identify a word or phrase that describes the central idea in each of the theories described above.
2. For each theory, describe the weakness that led to its being replaced.
3. What was the first theoretical definition of a base, and who developed it?
4. Write Lewis formulas for each substance in the reaction of boron trifluoride with ammonia, to illustrate the "electron pair transfer" concept.

Section 16.2 Questions

1. Aqueous solutions of nitric acid and nitrous acid of the same concentration are prepared.
   (a) Predict how their pH values compare.
   (b) Explain your answer using the Brønsted–Lowry concept.
2. Briefly state the five steps involved in predicting the predominant reaction and the approximate position of equilibrium in an acid–base reaction system.
3. According to the Brønsted–Lowry concept, what determines the position of equilibrium in an acid–base reaction?
4. What generalization from the table of Relative Strengths of Aqueous Acids and Bases (Appendix I) can be used to predict the position of an acid–base equilibrium?
5. State two examples of conjugate acid–base pairs, each involving the hydrogen sulfite ion.
6. Predict, with reasoning, including Brønsted–Lowry equations, whether each of the following chemical systems will be acidic, basic, or neutral.
   (a) aqueous hydrogen bromide
   (b) aqueous potassium nitrite
   (c) aqueous ammonia
   (d) aqueous sodium hydrogen sulfate
   (e) carbonated beverages
   (f) limewater
   (g) vinegar
7. Write an experimental design to test each of the predictions in question 6.
8. Write two experimental designs to rank a group of bases in order of strength.

9. Ammonia molecules and hydronium ions have remarkably similar shapes and structures (**Figure 18**). Both have three hydrogen atoms bonded in a pyramidal structure to a small central atom, which has one lone pair of electrons. Oxygen and nitrogen atoms both have very high electronegativities, and they are adjacent on the periodic table. Explain why an ammonia molecule is a good proton attractor, whereas a hydronium ion is an extremely poor proton attractor.

Figure 18
Evidence indicates that the ammonia molecule, NH_3, modelled here, has the same pyramidal shape as the hydronium ion, H_3O^+.

10. Many household cleaning solutions claim to "dissolve away" rust stains and hard water "lime" deposits (**Figure 19**). These cleaners are simply acidic solutions (as is vinegar) that react with slightly soluble substances such as $Fe_2O_3(s)$ and $CaCO_3(s)$. The word "react," however, sounds dangerous to consumers, and is hardly ever used in advertising. These cleaning solutions *must* be used carefully, and you should *always* read *all* of the label instructions, or you may find the cleaner also reacting with the item you are trying to clean, or even with you!

Figure 19
Commercial rust removing solutions must be used with care, but can be a very effective illustration of the old TV slogan, "better living, through chemistry."

These cleaners have a variety of formulations, but most contain hydroxyacetic acid (glycolic acid), $CH_2OHCOOH(aq)$. A 0.10 mol/L glycolic acid solution is 3.9% ionized at 25 °C, compared to 0.10 mol/L acetic acid, which is 1.3% ionized at the same temperature.

(a) Write a Brønsted–Lowry equation for the reaction of aqueous glycolic acid with carbonate ions (from hard water "scum"), and label both conjugate acid–base pairs.

(b) Explain whether the equilibrium would favour products more, or less, if acetic acid (vinegar) were used to do the same cleaning job. Is it likely that any difference would be significant? State your reasoning.

(c) Explain whether glycolic acid would react with a given chemical amount of rust more quickly or more slowly than an equal volume of equally concentrated acetic acid solution.

(d) Explain whether glycolic acid would react with a greater, or lesser, chemical amount of rust than an equal volume of equally concentrated acetic acid solution.

11. Since ancient times, people have known that strong heating of natural limestone (calcium carbonate) will produce quicklime (calcium oxide). This very useful substance is both reactive and corrosive with many organic substances because it has a high affinity for water. Adding water to quicklime causes the formation of slaked lime (calcium hydroxide)—the common name was derived from the idea that the lime was "slaking" its thirst. This reaction also produces a very considerable quantity of heat!

(a) Write a balanced chemical equation for the decomposition of calcium carbonate to carbon dioxide and calcium hydroxide.

(b) Write a balanced chemical equation for the addition of water to solid calcium oxide to produce solid calcium hydroxide.

(c) Write a Brønsted–Lowry equation for the instantaneous and quantitative (and highly exothermic) reaction of aqueous oxide ions with water.

Acid–Base Strength and the Equilibrium Law 16.3

Modifying Arrhenius' original concept of acids and bases allowed us to explain the behaviour of many substances in solution that could not be explained by his original theory. Then, problems with varying degrees of properties led to considering reactions of acids and bases as examples of equilibrium, which allowed a much more comprehensive understanding of relative acid or base strengths. Apparent conflicts in the definition of acids and bases then led us to define them by *what they do in a reaction* (in terms of proton transfer), rather than by *what they are* (in terms of some typical structure). This process of continually testing (identifying problems) and then expanding and improving concepts is typical of science—with the goal always being the formation of a more complete and comprehensive theory. Science assumes that no theory ever formed by the human mind can be "perfect," and that any theory, no matter how well supported by evidence, must always be questioned and tested. We also realize that every step moves us closer to a more complete understanding. Testing, and then restricting, revising, and (perhaps) replacing concepts, and then testing again is the constant cycle of the scientific method. Next, we explore the possible value of using the equilibrium law to further increase our understanding of acid–base behaviours.

The Acid Ionization Constant, K_a

One important way that chemists communicate the strength of any weak acid is by using the equilibrium constant expression for a Brønsted–Lowry reaction equation showing the acid ionizing in (reacting with) water. This expression is another very important *special case* of equilibrium. The constant is given its own unique name and symbol: the **acid ionization constant, K_a**. See the K_a values listed in the Relative Strengths of Aqueous Acids and Bases data table (Appendix I).

Note that in this table, the first six acids have K_a values given only as "very large." These acids are collectively called the *strong* acids because they all react quantitatively (>99.9%) with water to form hydronium ions. Because no acid stronger than $H_3O^+(aq)$ can exist in aqueous solution, all of these acids are considered equivalent. For each of them, the actual acid species present is $H_3O^+(aq)$.

All of the other acids listed on the table are considered to be *weak* acids, and they vary greatly in extent of reaction with water at equilibrium. To empirically rank any weak acid as stronger or weaker than any other, we normally compare the ionization of solutions *of the same concentration*, to see which is more strongly acidic (has a lower pH). This is how Appendix I was created.

By considering the equilibrium established in solutions of weak acid to be a Brønsted–Lowry proton transfer, we gain a more complete understanding about what is actually going on among the entities reacting. By using K_a equilibrium constants, we can derive and predict quantities that are very useful when working with acid–base reactions. Consider a solution of hydrofluoric acid, HF(aq). The equation for the reaction in water (ionization) of this weak acid is

$$HF(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + F^-(aq)$$

The equilibrium law expression is

$$K_a = \frac{[H_3O^+(aq)][F^-(aq)]}{[HF(aq)]}$$

Note that the concentration of liquid water is omitted from the K_a equilibrium law expression. We make an assumption that this value will remain *essentially* constant for

EXTENSION

Acid–Base Reactions

This quick simulation lets you explore the percent reaction when various acids and bases react together. The acid ionization constants are provided for two strong and three weak acids.

www.science.nelson.com GO

Learning Tip

Use of ionization terminology (*strong* and *weak*) can create a problem, caused by the common use of the word "strong." For an acid, *strength* refers only to the ease with which a base can remove its proton, and has nothing to do with the quantity present in the solution. *Concentration* refers to the chemical quantity per unit volume of solution, and has nothing to do with strength.

Both the strength and the concentration of an acid affect how rapidly, and to what extent, that acid will react.

Learning Tip

The great advantage of K_a values over percent ionization values is that, once determined, K_a values are valid over a wide range of acid solution concentrations. A percent ionization value is useful *only* for one specific concentration of one specific weak acid.

aqueous solutions *that are not highly concentrated*. This assumption is not *exactly* true, because the water is not a separate liquid phase in an aqueous solution. However, as long as the amount of water solvent is *much greater* than the amount of acid solute, making this assumption will cause negligible change in (and will not add uncertainty to) the answers for any calculations.

All K_a values are calculated by making this assumption. For this reason (and for other measurement reasons too involved to explain here), K_a values are necessarily somewhat inaccurate, and become less accurate as the acid concentration increases. It is important to know that K_a values given in tables are normally given to only two significant digits *because* they are usually only known to a certainty of about ± 5%.

Two calculations involving the K_a constant are common for weak acid solutions:

- calculating a K_a value from measured (empirical) amount concentration data
- using a K_a value to predict a concentration of hydronium ions for an aqueous solution where the initial weak acid amount concentration is known

Calculating K_a from Amount Concentrations

SAMPLE problem 16.2

The pH of a 1.00 mol/L solution of acetic acid is carefully measured to be 2.38 at SATP. What is the value of K_a for acetic acid?

Use the balanced equation to write the equilibrium law expression.

$$CH_3COOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

First, find the equilibrium concentration of aqueous hydronium ion from the pH.

$$[H_3O^+(aq)] = 10^{-pH}$$
$$= 10^{-2.38}$$
$$= 0.0042 \text{ mol/L}$$

Next, use the hydronium ion concentration and the balanced chemical equation to calculate the concentration of the acetate ion. Since one acetate ion forms for each hydronium ion, the equilibrium concentration of acetate ion must be identical to that of the hydronium ion. The stoichiometric ratio is 1:1.

$$[CH_3COO^-(aq)] = [H_3O^+(aq)] = 0.0042 \text{ mol/L}$$

An ICE table is useful to find the equilibrium concentration of acetic acid molecules.

Table 1 ICE Table for $CH_3COOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$

Concentration	$[CH_3COOH(aq)]$ (mol/L)	$[H_3O^+(aq)]$ (mol/L)	$[CH_3COO^-(aq)]$ (mol/L)
Initial	1.00	0	0
Change	− 0.0042	+ 0.0042	+ 0.0042
Equilibrium	1.00	0.0042	0.0042

$$K_a = \frac{(0.0042 \text{ mol/L})(0.0042 \text{ mol/L})}{(1.00 \text{ mol/L})}$$
$$= 0.000\,017$$

Regardless of numerical size, K_a values are usually expressed in scientific notation. The calculated K_a for acetic acid is 1.7×10^{-5}.

Learning Tip

Because the value for the initial acid concentration is precise only to two decimal places, the calculation of the *equilibrium* concentration of the acid (1.00 mol/L − 0.0042 mol/L) *rounds* to 1.00 mol/L. (See the Precision Rule for Calculations, Appendix F.3.) In other words, the decrease in the initial acid concentration is negligible, *in this particular case*. A negligible change in concentration is *quite often* the case for K_a calculations for weak acids, *but not always*.

Recall that amount concentrations must be used to calculate any K_c value and, by convention, units for the equilibrium constant value are simply ignored.

COMMUNICATION example 1

A student measures the pH of a 0.25 mol/L solution of carbonic acid to be 3.48. Calculate the K_a for carbonic acid from this evidence.

Solution

$$H_2CO_3(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HCO_3^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][HCO_3^-(aq)]}{[H_2CO_3(aq)]}$$

At equilibrium,

$$[H_3O^+(aq)] = 10^{-pH}$$
$$= 10^{-3.48}$$
$$= 3.3 \times 10^{-4} \text{ mol/L}$$

$$[HCO_3^-(aq)] = [H_3O^+(aq)] = 3.3 \times 10^{-4} \text{ mol/L}$$

$$[H_2CO_3(aq)] = (0.25 - 0.000\,33) \text{ mol/L}$$
$$= 0.25 \text{ mol/L}$$

Table 2 ICE Table for $H_2CO_3(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HCO_3^-(aq)$

Amount concentration	$[H_2CO_3(aq)]$ (mol/L)	$[H_3O^+(aq)]$ (mol/L)	$[HCO_3^-(aq)]$ (mol/L)
Initial	0.25	0	0
Change	− 0.000 33	+ 0.000 33	+ 0.000 33
Equilibrium	0.25	0.000 33	0.000 33

$$K_a = \frac{(0.000\,33 \text{ mol/L})(0.000\,33 \text{ mol/L})}{(0.25 \text{ mol/L})} = 0.000\,000\,44$$

According to the equilibrium law, the K_a for carbonic acid is 4.4×10^{-7}.

Learning Tip

Because a Brønsted-Lowry equation is written to show a single proton transfer, the stoichiometric ratio will always be 1:1:1:1. Thus, the units for K_a values will always be mol/L. Because we can make this assumption, units are often not included with K_a values in reference tables or in final answer statements.

COMMUNICATION example 2

The pH of a 0.400 mol/L solution of sulfurous acid is measured to be 1.17.

Calculate the K_a for sulfurous acid from this evidence.

Solution

$$H_2SO_3(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HSO_3^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][HSO_3^-(aq)]}{[H_2SO_3(aq)]}$$

At equilibrium,

$$[H_3O^+(aq)] = 10^{-pH}$$
$$= 10^{-1.17}$$
$$= 0.068 \text{ mol/L}$$

$$[HSO_3^-(aq)] = [H_3O^+(aq)] = 0.068 \text{ mol/L}$$

$$[H_2SO_3(aq)] = (0.400 - 0.068) \text{ mol/L}$$
$$= 0.332 \text{ mol/L}$$

Table 3 ICE Table for $H_2SO_3(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HSO_3^-(aq)$

Amount concentration	$[H_2SO_3(aq)]$ (mol/L)	$[H_3O^+(aq)]$ (mol/L)	$[HSO_3^-(aq)]$ (mol/L)
Initial	0.400	0	0
Change	− 0.068	+ 0.068	+ 0.068
Equilibrium	0.332	0.068	0.068

$$K_a = \frac{(0.068 \text{ mol/L})(0.068 \text{ mol/L})}{(0.332 \text{ mol/L})} = 0.014$$

According to the equilibrium law, the K_a for sulfurous acid is 1.4×10^{-2}.

Calculating $[H_3O^+(aq)]$ from K_a

The second type of calculation involving a K_a value allows us to *predict* the acidity of any weak acid solution. We can calculate the concentration of hydronium ions from the initial acid concentration and the K_a value as follows.

SAMPLE problem 16.3

Predict the $[H_3O^+(aq)]$ and pH for a 0.200 mol/L aqueous solution of methanoic acid.

Look up the value of K_a for methanoic (formic) acid in the Relative Strengths of Aqueous Acids and Bases data table (Appendix I). The value is given as 1.8×10^{-4}.

Use the balanced equation to write the equilibrium law expression.

$$HCOOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HCOO^-(aq)$$

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+(aq)][HCOO^-(aq)]}{[HCOOH(aq)]}$$

Use x to represent *the numerical value* for the equilibrium amount concentration of aqueous hydronium ions.

$[H_3O^+(aq)] = x$ mol/L

An ICE table is useful to keep track of the concentration values.

Using the 1:1:1:1 stoichiometric ratio, calculate concentration increases and decreases for the reaction to equilibrium, and note them in the ICE table.

Table 4 ICE Table for $HCOOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HCOO^-(aq)$

Concentration	$[HCOOH(aq)]$ (mol/L)	$[H_3O^+(aq)]$ (mol/L)	$[HCOO^-(aq)]$ (mol/L)
Initial	0.200	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(0.200 - x)$*	x	x

Substituting into the equilibrium law expression, ignoring units,

$$1.8 \times 10^{-4} = \frac{[H_3O^+(aq)][HCOO^-(aq)]}{[HCOOH(aq)]}$$

$$= \frac{(x)(x)}{(0.200 - x)}$$

*** Note**:
Technically, solving for x (the amount concentration of hydronium ion) from this expression requires the use of the quadratic formula, $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$, which is quite tedious, unless you have a calculator that is preprogrammed to solve such formulas.

Conveniently, for many (but not all) weak acid solutions, we can use an approximation that greatly simplifies solving for x. If the percent reaction of the weak acid is quite small, we can assume that the initial concentration of the acid decreases by so little that the numerical value of the acid amount concentration will remain effectively unchanged at equilibrium.

The problem, of course, is deciding when a percent reaction is small enough to allow this assumption to be used. In this text, we will apply the mathematically simplest (and most convenient) "rule of thumb" that is commonly used to make this decision.

> *If the initial amount concentration of the acid is numerically at least 1000 times its K_a value, then you may assume that the initial and equilibrium acid amount concentrations are numerically equal.*

This limiting assumption is consistent with the $\pm 5\%$ certainty of most K_a values, meaning it ignores those amount concentration changes that would change the K_a value by less than the uncertainty that already exists.

Note that the equation to be solved contains a squared value.

$$0.000\ 18 = \frac{x^2}{(0.200 - x)}$$

Multiplying both sides by $(0.200 - x)$, collecting terms, and equating to zero gives $x^2 + 0.000\ 18x - 0.000\ 036 = 0$ (expressed in the form of a quadratic equation).

Notice what happens when we test our present example for the simplifying assumption.

$$\frac{[HCOOH(aq)]_{initial}}{K_a} = \frac{0.200}{0.000\ 18} = 1111, \text{ which is greater than } 1000$$

The test allows us to use the assumption (initial acid concentration = equilibrium acid concentration, or $[HA(aq)]_{initial} = [HA(aq)]_{equilibrium}$). In this specific case, so little acid has reacted with water at equilibrium that the initial acid concentration is decreased by a negligible amount—less than the uncertainty of the initial value.

Numerically, for this example, we may assume that $(0.200 - x) = 0.200$, and we can then simplify the equation to

$0.000\ 18 = \frac{x^2}{0.200}$, which makes solving for x quick and easy.

Isolate x and take the square root of both sides of the equation:

$$x = \sqrt{0.000\ 18 \times 0.200}$$
$$= 0.0060$$

so, $[H_3O^+(aq)] = 0.0060$ mol/L or 6.0×10^{-3} mol/L

and $pH = -\log [H_3O^+(aq)]$
$= -\log (0.0060)$
$= 2.22$

DID YOU KNOW ?

Rule of Thumb

The very old English phrase "rule of thumb," meaning a rule for any quick way to approximate a quantity without measuring, probably comes directly from use of human thumbs. Since the width of an adult's thumb is approximately one inch, and the length of a thumb is approximately four inches, you can make a fairly good estimate of the length of something (in Imperial units) by simply placing your thumbs along the object, one after the other. What is the length of this textbook in (your) thumb widths? What do equestrians mean when they say a horse stands 16 "hands" high?

A practical rule of thumb for Americans driving their cars into Mexico or Canada is to multiply the posted speed by 6 and drop the last digit, in order to quickly convert the km/h speeds on road signs into a fairly close miles-per-hour equivalent.

DID YOU KNOW ?

pK_a

For purposes of easy comparison, the K_a values of different acids are sometimes expressed as pK_a values. A pK_a value is the negative logarithm of the K_a. A reported pK_a value of 12 would represent an acid with a K_a of 1×10^{-12}, a very weak acid. In comparing any two weak acids, the one with the lower pK_a value is the stronger of the two acids.

As shown in the next Communication Example, when the negligible ionization (percent reaction) assumption holds true, predictions of $[H_3O^+(aq)]$ using K_a values become simple and straightforward. Note that you can perform the 1000:1 ratio test for the simplifying assumption *before starting the problem*, which is very convenient.

COMMUNICATION example 3

Predict the $[H_3O^+(aq)]$ and pH for a 0.500 mol/L aqueous solution of hydrocyanic acid.

Solution

Test the simplifying assumption:

$$\frac{[HCN(aq)]_{initial}}{K_a} = \frac{0.500}{6.2 \times 10^{-10}} = 8.1 \times 10^7 \text{ (greater than 1000)}$$

The assumption holds, and may be used.

$$K_a = 6.2 \times 10^{-10} = \frac{[H_3O^+(aq)][CN^-(aq)]}{[HCN(aq)]}$$

At equilibrium:

Let $x = [H_3O^+(aq)] = [CN^-(aq)]$

Then $[HCN(aq)] = (0.500 - x) = 0.500$ (using the assumption)

Table 5 ICE Table for $HCN(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CN^-(aq)$

Amount concentration	[HCN(aq)] (mol/L)	$[H_3O^+(aq)]$ (mol/L)	$[CN^-(aq)]$ (mol/L)
Initial	0.500	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(0.500 - x) = 0.500$	x	x

$$6.2 \times 10^{-10} = \frac{x^2}{0.500}$$

$$x = \sqrt{6.2 \times 10^{-10} \times 0.500} = 1.8 \times 10^{-5}$$

so, $[H_3O^+(aq)] = 1.8 \times 10^{-5}$ mol/L

and $pH = -\log [H_3O^+(aq)] = -\log (1.8 \times 10^{-5}) = 4.75$

According to the equilibrium law, the hydronium ion amount concentration of 0.500 mol/L hydrocyanic acid is 1.8×10^{-5} mol/L, and the pH of the solution is 4.75.

Note: No Practice, Section, or Review question in this text will require you to use the quadratic formula to solve acid ionization constant problems. However, you may be asked to state whether a given problem would require use of this formula for solution (in other words, whether the ionization assumption test fails). You should develop the habit of always initially testing the assumption and making a qualifying statement before completing the solution to any K_a question where this assumption holds.

Practice

1. (a) Write a *theoretical* definition for the strength of an acid.
(b) State the *empirical* properties that provide evidence for differing acid strengths.
(c) Explain the difference in meaning between *strength* and *concentration*, as these terms are used to refer to aqueous acids.
(d) Does the stronger of two acids, when dissolved, necessarily make a more acidic aqueous solution? Explain.

2. Refer to Appendix I for required information to make the following predictions. For each case, first decide and state whether a solution would require use of the quadratic formula. For all cases where use of the quadratic formula is *not* required, communicate the full solution.
(a) Predict $[H_3O^+(aq)]$ for 0.20 mol/L hydrobromic acid.
(b) Predict $[H_3O^+(aq)]$ for 0.20 mol/L hydrofluoric acid.
(c) Predict $[H_3O^+(aq)]$ for 0.20 mol/L ethanoic acid.
(d) Predict the pH of 2.3 mmol/L nitric acid.
(e) Predict the pH of 2.3 mmol/L nitrous acid.
(f) Predict the pH of 2.3 mmol/L hydrosulfuric acid.

3. For all of the cases (a–f) in question 2 *where a prediction could be calculated*, rank the acid solutions in order of decreasing acidity.

4. For all of the cases (a–f) in question 2, rank the acids in order of decreasing acid strength. Which two acids have essentially the same strength?

5. The hydronium ion concentration in 0.100 mol/L propanoic acid is determined (from a pH measurement) to be 1.16×10^{-3} mol/L.
(a) Calculate the percent reaction (ionization) of this particular weak acid solution.
(b) Calculate K_a for aqueous propanoic acid.
(c) Is this K_a value constant for propanoic acid? Explain.

6. A 0.10 mol/L solution of lactic acid, a weak acid found in milk, has a measured pH of 2.43. The chemical name for this very common organic compound is 2-hydroxypropanoic acid.
(a) Find the percent reaction of this lactic acid solution.
(b) Calculate the K_a value for aqueous lactic acid.
(c) Compare the K_a values for 2-hydroxypropanoic acid and for propanoic acid. What effect does adding an OH group to the central carbon atom of this molecule have on the ability of the COOH group to attract a proton?

7. Unlike all other aqueous hydrogen halides, hydrofluoric acid is not a strong acid. It does, however, have a special chemical property: it reacts with glass. This property is used to etch frosted patterns on glassware (**Figure 1**).
(a) Write the K_a expression for hydrofluoric acid.
(b) Calculate the hydronium and fluoride ion amount concentrations, the pH, and the percent reaction in a commercial 2.0 mol/L HF(aq) solution at 25 °C.

8. Phosphoric acid is used in rust-remover solutions. The aqueous acid is available for purchase by high schools in concentrations of about 15 mol/L.
(a) Predict the hydronium ion amount concentration, the pH, and the percent reaction of a 10 mol/L solution of phosphoric acid.
(b) Suggest a reason (having to do with K_a values and solution concentrations) why you might well suspect that these values could be inaccurate.

9. Ascorbic acid is the chemical name for Vitamin C (**Figure 2**). A student prepares a 0.200 mol/L aqueous solution of ascorbic acid, tests its pH, and reads a value of 2.40 from the pH meter.
(a) From the student's evidence, calculate the K_a for ascorbic acid.
(b) Compare your result to the value listed in the table of Relative Strengths of Aqueous Acids and Bases (Appendix I). The K_a value for ascorbic acid increases with increasing temperature. State whether the student's aqueous solution was likely warmer or colder than standard temperature (25 °C) when the pH was tested.

Figure 1
Hydrofluoric acid is a weak acid but it etches glass. The etching is not due to the presence of hydronium ions, because, as you know, even the strongest acids are routinely stored in glass containers.

Figure 2
Vitamin C (ascorbic acid) is present in many fresh foods, particularly citrus fruits. It is essential to the body to promote healing of injuries and to fight infection.

In the winter of 1535, the men of Jacques Cartier's expedition were suffering from scurvy (vitamin C deficiency) in their fort at Stadacona (now Montreal). Cartier lost 25 men before learning of a simple cure from the Iroquois. The Aboriginal people prepared a tea made from white cedar needles—rich in ascorbic acid—that cured sufferers within days.

DID YOU KNOW ?

Sailors and Scurvy

Vitamin C deficiency (from a dietary lack of fresh fruits and vegetables) causes scurvy, a disease where the body cannot fight infections, and cuts, sores, and bruises do not heal. Until the last half of the 18th century, this disease was a terrible problem for sailors, and a major cause of death on long voyages. For example, on his famous voyage of 1498, Vasco da Gama lost 100 of 160 crewmen to scurvy. The diet of European sailors was primarily salted meat and hard biscuits—items selected for their resistance to spoilage.

In 1747, James Lind, a Scottish physician, wrote that feeding citrus fruit to scurvy victims effected an amazingly rapid cure. Captain Cook tried this remedy on his crew during his famous voyages of exploration in the 1770s, and reported that he was astounded to have lost only one man on a three-year voyage!

By 1795, the British Royal Navy (after decades of deliberation) formally adopted the practice of providing lemon juice (incorrectly referred to as lime juice) for all hands. Scurvy in the fleet was wiped out, and British sailors have been called "limeys" ever since.

Note that this story illustrates another case of technology leading science: The cure for scurvy was known long before the cause of the disease was explained.

Interestingly, sailors on the long sea voyages undertaken by the Chinese during the Ming Dynasty (1368–1644) had no problems with scurvy because their traditional diet included fresh germinated soya beans, the shoots of which are naturally rich in Vitamin C.

Base Strength and the Ionization Constant, K_b

The Brønsted–Lowry concept specifies that the strongest base possible in aqueous solution must be hydroxide ions. So, hydroxide ion is considered to be "the" strong base—somewhat parallel to the strong acids. A difference is that many ionic substances contain hydroxide ions initially, before being dissolved; whereas hydronium ions are always formed by the reaction of some entity with water, after a substance dissolves. Recall that for solutions of all ionic hydroxides, such as $NaOH(aq)$ or $Ca(OH)_2(aq)$, we assume that the compound dissociates completely upon dissolving. Therefore, finding the hydroxide ion concentration does not involve any reaction with water or any reaction equilibrium. Rather, in these cases, we find the hydroxide ion concentration directly from a dissociation equation, as shown in the next Communication Example.

COMMUNICATION example 4

Find the hydroxide ion concentration of a 0.064 mol/L solution of barium hydroxide.

Solution

$$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\,OH^-(aq) \text{ (complete dissociation)}$$

$$[OH^-(aq)] = [Ba(OH)_2(aq)] \times \frac{2}{1}$$

$$= 0.064 \text{ mol/L} \times \frac{2}{1}$$

$$= 0.13 \text{ mol/L}$$

According to the stoichiometric ratio, the hydroxide ion concentration is 0.13 mol/L.

Other entities that act as bases are collectively called weak bases, because empirical evidence indicates that they attract protons less than hydroxide ions do. Turn to the table of Relative Strengths of Aqueous Acids and Bases (Appendix I), and observe that, to the right of every acid entity formula listed, there is a formula for an entity that is identical to the acid's formula, *except* that one proton (represented as H^+) is missing. As you have learned, such an entity is called the conjugate base of the acid. While the list of these entities (reading upward) can be taken to be a list of bases and their (decreasing) relative strengths, note that there is no corresponding value given to show the extent of reaction of these entities with water. This convention is common in chemistry—information about bases in solution must be derived from a table of acid values.

Bases vary in strength much as acids do, and the system used to identify, classify, and rank the strength of bases is quite similar to the one you have just learned for acids. Note that the table in Appendix I shows that the weaker an acid is, the stronger its conjugate base (and vice versa). This observation is common sense. If it is very easy to remove the proton from an acid, then the entity remaining (the conjugate base) must not attract protons very well.

As you know, weak bases react only partially (usually much less than 50%) with water in aqueous solution to produce hydroxide ions. We can communicate the strength of any weak base using the equilibrium constant expression for its reaction with water in dilute aqueous solution. This equilibrium constant for weak bases is another special case, where the K_c constant is called the **base ionization constant, K_b**.

Consider a solution of sodium citrate, $Na_3C_6H_5O_7(aq)$. We assume that in aqueous solution, any ionic compound dissociates completely into its component ions. In this case,

the ions are aqueous sodium and citrate ions: $Na^+(aq)$ and $C_6H_5O_7^{3-}(aq)$. Sodium ions are "spectators," with no apparent acidic or basic properties. The citrate ions, however, are found on the Relative Strengths of Aqueous Acids and Bases data table (Appendix I) in the conjugate bases column. So the citrate ion is a weak Brønsted–Lowry base and reacts with water to form a basic solution at equilibrium.

The reaction equilibrium equation for aqueous sodium citrate is

$$C_6H_5O_7^{3-}(aq) + H_2O(l) \rightleftarrows HC_6H_5O_7^{2-}(aq) + OH^-(aq)$$

The equilibrium law expression is

$$K_b = \frac{[HC_6H_5O_7^{2-}(aq)][OH^-(aq)]}{[C_6H_5O_7^{3-}(aq)]}$$

Just as with K_a values, there are two kinds of weak base solution calculations that involve the K_b constant:

- calculating a K_b value from empirical (measured) amount concentration data
- using a K_b value to predict an amount concentration of hydroxide ions for an aqueous solution where the initial weak base concentration is known

Learning Tip

The concentration of liquid water is omitted from K_b equilibrium law expressions for the same reasons that it is omitted from K_a expressions. As with K_a values, K_b values are also only certain to about ±5%. For weak base K_b values, we also assume that aqueous solutions are not highly concentrated, just as we do for weak acids. Just as with K_a values, K_b value units are ignored, by convention.

Calculating K_b from Amount Concentrations

Calculating K_b for a weak base uses essentially the same method as calculating K_a for a weak acid. Often, an extra (simple) calculation step must be included because measured pH values may need to be converted to find the equilibrium hydroxide ion concentration, as shown in the following Communication Example.

COMMUNICATION example 5

A student measures the pH of a 0.250 mol/L solution of aqueous ammonia and finds it to be 11.32.

Calculate the K_b for ammonia from this evidence. Show the establishment of the reaction equilibrium using an ICE table.

Solution

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

At equilibrium:

$$[H_3O^+(aq)] = 10^{-pH}$$
$$= 10^{-11.32}$$
$$= 4.8 \times 10^{-12}\ mol/L$$

$$K_w = [H_3O^+(aq)][OH^-(aq)]$$

$$[OH^-(aq)] = \frac{K_w}{[H_3O^+(aq)]}$$
$$= \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-12}\ mol/L}$$
$$= 0.0021\ mol/L$$

$[NH_4^+(aq)] = [OH^-(aq)]$

$= 0.0021 \text{ mol/L}$

$[NH_3(aq)] = (0.250 - 0.0021) \text{ mol/L}$

$= 0.248 \text{ mol/L}$

Table 6 ICE Table for $NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$

Concentration	$[NH_3\ (aq)]$ (mol/L)	$[NH_4^+(aq)]$ (mol/L)	$[OH^-(aq)]$ (mol/L)
Initial	0.250	0	0
Change	− 0.0021	+ 0.0021	+ 0.0021
Equilibrium	0.248	0.0021	0.0021

$$K_b = \frac{[0.0021 \text{ mol/L}][0.0021 \text{ mol/L}]}{[0.248 \text{ mol/L}]} = 0.000\ 018$$

From this evidence, and according to the equilibrium law, the K_b for aqueous ammonia is 1.8×10^{-5}.

Figure 3
Dyes with molecular structures based on aniline make possible a variety of bright, stable colours for fabrics and leathers.

Practice

10. List some empirical properties that would be useful when distinguishing strong bases from weak bases.

11. For each of the following weak bases, write the chemical equilibrium equation and the equilibrium law expression for K_b.
(a) $CN^-(aq)$
(b) $SO_4^{2-}(aq)$

12. The hydroxide ion concentration in a 0.157 mol/L solution of sodium propanoate, $NaC_2H_5COO(aq)$, is found to be 1.1×10^{-5} mol/L. Calculate the base ionization constant for the propanoate ion.

13. Aniline, $C_6H_5NH_2$, is used to make a wide variety of drugs and dyes (**Figure 3**). It has the structure of an ammonia molecule, with a phenyl group substituted for one hydrogen, and, like ammonia, acts as a weak base. If the pH of a 0.10 mol/L aniline solution was found to be 8.81, what is its K_b?

Learning Tip

The use of chemical (IUPAC) and common names can be confusing if you have not memorized a few examples. In this textbook, the normal practice is to give the chemical name, followed by a common name in parentheses. A few substances are so widely used, however, that the common name is ubiquitous (used everywhere, even by chemists). Baking soda (sodium bicarbonate, sodium hydrogen carbonate) and vinegar (acetic acid, ethanoic acid) are two examples of such chemicals; the common name is often given, rather than the IUPAC name. You are expected to be familiar with such examples, and others listed in Appendix J.

Calculating $[OH^-(aq)]$ from K_b

The second type of calculation involving a K_b value is the *prediction* of the basicity of any weak base solution. We can calculate the concentration of hydroxide ions from the initial weak base concentration and the K_b value. There is an automatic problem, however, because tables of relative acid–base strengths do not normally list K_b values. We use the automatic relationship between conjugate acid–base pairs to deal with this problem.

The $K_a - K_b$ Relationship for Conjugate Acid–Base Pairs

To develop the next useful concept, we use the common weak acid, acetic acid, $CH_3COOH(aq)$, and its conjugate base, the acetate ion, $CH_3COO^-(aq)$. Of course, it would be just as correct to state that we will use the weak base, acetate ion, and its conjugate acid, acetic acid.

The equilibrium reaction and law expression for aqueous acetic acid are

$$CH_3COOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

For the weak base, aqueous acetate ion,

$$CH_3COO^-(aq) + H_2O(l) \rightleftarrows CH_3COOH(aq) + OH^-(aq)$$

$$K_b = \frac{[CH_3COOH(aq)][OH^-(aq)]}{[CH_3COO^-(aq)]}$$

Notice what happens when we multiply these equilibrium constant expressions:

$$K_a \times K_b = \frac{[H_3O^+(aq)]\cancel{[CH_3COO^-(aq)]}}{\cancel{[CH_3COOH(aq)]}} \times \frac{\cancel{[CH_3COOH(aq)]}[OH^-(aq)]}{\cancel{[CH_3COO^-(aq)]}}$$

$$= [H_3O^+(aq)][OH^-(aq)] \quad \text{(Does this expression look familiar?)}$$

$$= K_w$$

So, for any conjugate acid–base pair, $K_w = K_a K_b$ and $K_b = \frac{K_w}{K_a}$.

This last equation is particularly useful because now, to find a K_b value for any base listed on the Relative Strengths of Aqueous Acids and Bases table (Appendix I), you need only identify its conjugate acid, and then divide K_w, 1.0×10^{-14}, by the K_a value given for that conjugate acid.

SAMPLE problem 16.4

Solid sodium benzoate forms a basic solution. Determine K_b for the weak base present.

$NaC_6H_5COO(s) \rightarrow Na^+(aq) + C_6H_5COO^-(aq)$ (complete dissociation)

First identify, from the Relative Strengths of Aqueous Acids and Bases table, and the entities present in solution, which entity is reacting as a base.

The benzoate ion must be the weak base entity. Its equilibrium reaction with water is

$$C_6H_5COO^-(aq) + H_2O(l) \rightleftarrows C_6H_5COOH(aq) + OH^-(aq)$$

From the equilibrium equation, the conjugate acid of the benzoate ion is identified as benzoic acid. From the acid–base table,

K_a for $C_6H_5COOH(aq) = 6.3 \times 10^{-5}$

Using the K_w relationship for conjugate acid–base pairs, find K_b for $C_6H_5COO^-(aq)$.

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}}$$

$$= 1.6 \times 10^{-10}$$

According to the K_w relationship, the benzoate ion has a K_b value of 1.6×10^{-10}.

DID YOU KNOW ?

Why Acidity?

It should be obvious by now that pH values are used much more than pOH values, and K_a constants are listed in tables rather than K_b constants. You might wonder why we choose to emphasize the hydronium ion properties of aqueous solutions—after all, hydroxide ions play exactly the opposite (and an equally important) role. But historically, chemists have always been much more concerned with acidic properties than with basic properties. Acids dissolve (react with) many metals to form common ionic compounds and hydrogen. Hydrogen gas was a fascinating product to early chemists, both because it is lighter than air and because it is violently explosive. The stronger acids tend to have painfully sharp odours and flavours, and react destructively with human tissue—all properties that make acids quite noticeable. Even when it became clearly understood that acids and bases were opposite aspects of the same concept, it seemed easier to choose acid properties as the initial basis for studying acid–base relationships. We talk about the "acidity" of something routinely; it is a common term, found in any pocket dictionary. What is the equivalent term for how *basic* something is? There is an accepted word for it, but you'll need a *really* good (very big) dictionary to find it. Or a good Chemistry text, of course...

COMMUNICATION example 6

Calculate K_b for the weak base aqueous ammonia, commonly used in commercial window cleaning solutions. Write the equation for the equilibrium.

Solution

$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$

For $NH_3(aq)$, $NH_4^+(aq)$ is the conjugate acid:

$K_a = 5.6 \times 10^{-10}$

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}}$$

$$= 1.8 \times 10^{-5}$$

According to the table of Relative Strengths of Aqueous Acids and Bases, and the K_a–K_b relationship, the K_b value for aqueous ammonia is 1.8×10^{-5}.

Now we can easily predict how basic a solution of known concentration will be from its K_b value. Predicting basicity always involves calculating the hydroxide ion concentration, and may also involve calculating a value for pOH, pH, and/or percent reaction. The first step may be determining the K_b value by using a table of K_a values. The form of the calculation then follows the same format as the equivalent type of question for weak acids, with a similar assumption made, and the same restrictions.

- Assume that the initial weak base aqueous concentration decreases so little that it is numerically unchanged at equilibrium, but *only* if the initial amount concentration of the weak base is at least 1000 times greater than its K_b value.
- For questions in this text, you are not required to do calculations using the quadratic formula.

The Sample Problem that follows shows the format for calculations of this type, and also an example of each conversion that may be required.

Recall, from Section 16.2, that, in aqueous solution, the amphiprotic ion $HCO_3^-(aq)$ reacts with water as a base to a *very* much greater extent than it does as an acid. You may, therefore, assume that the solution is basic because the ion reacts as a base, and ignore its negligible reaction extent as an acid.

SAMPLE problem 16.5

Find the hydroxide ion amount concentration, pOH, pH, and percent reaction (ionization) of a 1.20 mol/L solution of baking soda.

The compound is sodium hydrogen carbonate, $NaHCO_3(s)$. The weak base is the $HCO_3^-(aq)$ ion, produced by dissolving $NaHCO_3(s)$ in water.

For $HCO_3^-(aq)$, $H_2CO_3(aq)$ is the conjugate acid:

$K_a = 4.5 \times 10^{-7}$

Find the K_b value using the K_a–K_b–K_w relationship.

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-7}}$$

$$= 2.2 \times 10^{-8}$$

Write the equation for the reaction and the equilibrium expression for K_b for hydrogen carbonate ion.

$$HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$$

$$K_b = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]}$$

At equilibrium, let x be the numerical value of $[OH^-(aq)]$ and also $[H_2CO_3(aq)]$.

Table 7 ICE Table for $HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$

Amount concentration	$[HCO_3^-(aq)]$ (mol/L)	$[H_2CO_3(aq)]$ (mol/L)	$[OH^-(aq)]$ (mol/L)
Initial	1.20	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(1.20 - x)$	x	x

Then $[HCO_3^-(aq)] = (1.20 - x)$

Test the assumption that $(1.20 - x)$ is numerically equal to 1.20.

$$\frac{[HCO_3^-(aq)]_{initial}}{K_b} = \frac{1.20}{2.2 \times 10^{-8}} = 5.5 \times 10^7 \text{ (much greater than 1000)}$$

The assumption holds, so substitute into the K_b expression and solve for x.

$$2.2 \times 10^{-8} = \frac{x^2}{1.20}$$

$$x = \sqrt{2.2 \times 10^{-8} \times 1.20}$$

$$= 1.6 \times 10^{-4}$$

$$[OH^-(aq)] = 1.6 \times 10^{-4} \text{ mol/L}$$

Use $[OH^-(aq)]$ to find the value of pOH.

$$pOH = -\log [OH^-(aq)]$$

$$= -\log (1.6 \times 10^{-4})$$

$$= 3.80$$

Use the pOH value to find pH.

$$pH = 14.00 - pOH$$

$$= 14.00 - 3.80$$

$$= 10.20$$

Percent reaction is the percent ratio of the equilibrium concentration of produced hydroxide ions to the initial concentration of hydrogen carbonate ions.

$$\text{percent reaction} = \frac{[OH^-(aq)]_{equilibrium}}{[HCO_3^-(aq)]_{initial}} \times 100\%$$

$$= \frac{1.6 \times 10^{-4} \text{ mol/L}}{1.20 \text{ mol/L}} \times 100\%$$

$$= 0.013\%$$

A 1.20 mol/L sodium hydrogen carbonate solution has a hydroxide ion concentration of 1.6×10^{-4} mol/L, a pOH of 3.80, a pH of 10.20, and a percent reaction of 0.013%.

The Effect of Amphoteric Entities

Finally, we deal with the problem of amphoteric entities. If an entity can react as either a Brønsted–Lowry acid or base, how do you know which will be the predominant reaction in its aqueous solution? You can determine the answer with one simple calculation.

DID YOU KNOW ?

Visualizing Reaction Extents

From any percent reaction value, you can get a better idea of the reaction extent at equilibrium by converting mentally to a whole-number ratio. If bicarbonate ions react with water 0.013% at equilibrium, the ratio is 0.013:100, or 13:100 000. This means that at any given instant, about 13 of every 100 000 initial bicarbonate ions have changed to carbonic acid molecules, but 99 987 of them have not. The few ions that have changed are responsible for all the basicity of the solution!

If you *really* want to test your powers of imagination, try to visualize that for every 100 000 bicarbonate ions in this aqueous solution, there are approximately 5 500 000 water molecules. Now think about all of these entities constantly moving at speeds averaging about 1500 km/h, and then imagine every one of them colliding with another molecule or ion at a rate of approximately 7 000 000 000 times *every second*…

Figure 4
Codeine (methylmorphine, $C_{18}H_{21}NO_3$) is available by prescription as an ingredient in some analgesic (pain relief) medicines. This narcotic alkaloid was initially extracted from opium. Other alkaloids include nicotine, quinine, cocaine, strychnine, and caffeine. All are common plant-derived organic compounds based on nitrogen-containing ring structures.

Read the K_a value for the entity from the table of Relative Strengths of Aqueous Acids and Bases. Calculate the K_b value for the entity from K_w and the K_a value (from the table) of its conjugate acid, as shown in Sample Problem 16.5. The higher of the "K" values tells you which reaction predominates, and, therefore, whether the entity reacts as an acid or as a base in aqueous solution.

COMMUNICATION example 7

Which reaction predominates when $NaHSO_3(s)$ is dissolved in water to produce $HSO_3^-(aq)$ solution? Will the solution be acidic or basic?

Solution

$K_a = 6.3 \times 10^{-8}$

The conjugate acid is $H_2SO_3(aq)$, with $K_a = 1.4 \times 10^{-2}$.

So, for $HSO_3^-(aq)$,

$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-2}}$$

$$= 7.1 \times 10^{-13}$$

The K_a value for $HSO_3^-(aq)$ far exceeds its calculated K_b value.

According to the K_w relation and the equilibrium law, an aqueous solution of this substance will be acidic because a hydrogen sulfite ion will react predominately as a Brønsted–Lowry acid.

Section 16.3 Questions

1. Codeine, an ingredient in these migraine pills (**Figure 4**), has a K_b of 1.73×10^{-6}. Calculate the pH of a 0.020 mol/L codeine solution (use Cod as a chemical shorthand symbol for this complex weak base entity.).
2. What is the pH of a 0.18 mol/L cyanide ion solution?
3. Acetylsalicylic acid (ASA) is a painkiller used in many headache tablets. This drug forms an acidic solution that attacks the digestive system lining. *The Merck Index* lists its K_a at 25 °C to be 3.27×10^{-4}. Explain the difficulty in calculating the pH of a saturated 0.018 mol/L solution of acetylsalicylic acid, $C_6H_4COOCH_3COOH(aq)$.
4. Boric acid is used for weatherproofing wood and fireproofing fabrics. Very dilute aqueous boric acid is used in eyewash solution as a preservative. Predict the pH of a 0.50 mol/L solution of boric acid.
5. Salicylic acid (2-hydroxybenzoic acid, $C_6H_5OHCOOH(s)$) is an active ingredient of medications, such as Clearasil®, that are used to treat acne. Since the K_a for this acid was not listed in any convenient references, a student tried to determine the value experimentally. She kept adding water slowly to a 1.00 g sample, with constant stirring, until the crystals all dissolved. The volume of solution was 460 mL. She found that the pH of this solution of salicylic acid was 2.40 at 25 °C. Calculate the ionization constant for this acid.
6. Sodium hydrogen ascorbate is often used as an antioxidant in packaged non-fat foods. The pH of a 0.15 mol/L laboratory solution of sodium hydrogen ascorbate, $NaHC_6H_6O_6(aq)$ is measured to be 8.65. From this evidence, calculate the K_b value for the hydrogen ascorbate ion.
7. Sodium hypochlorite is a strong oxidizing agent that is a fire hazard when in contact with organic materials. Solutions of sodium hypochlorite are used as bleach and disinfectant. Determine the hydroxide ion amount concentration of a sodium hypochlorite solution sold as household bleach. The bleach bottle label reads "5.25% (by mass) when packed."
8. Write the equilibrium law expression for acetic acid reacting (ionizing) in water. Use Le Châtelier's principle to explain, in terms of equilibrium shift, why dilute acetic acid solutions have a higher percent reaction than more concentrated solutions. Consider that diluting a solution containing reacting aqueous entities is very similar to increasing the volume of a container of reacting gaseous entities.
9. Predict and write the predominant Brønsted–Lowry reaction in aqueous solutions of the following substances:
   (a) $K_2HPO_4(s)$ (b) $NaH_2PO_4(s)$ (c) $Na_2HC_6H_5O_7(s)$
10. Calculate the pH of 5.0×10^{-2} mol/L solutions of each of the reagents in question 9.

Interpreting pH Curves 16.4

For many acid–base reactions, the appearance of the products resembles that of the reactants, so we cannot directly observe the progress of a reaction. Also, acids cannot easily be distinguished from bases except by measuring pH. As you first learned in Chapter 8, a graph showing the continuous change of pH during an acid–base titration, continued until the titrant is in great excess, is called a **pH curve** (titration curve) for the reaction. The pH values and changes provide important information about the nature of acids and bases, the properties of conjugate acid–base pairs and indicators, and the stoichiometric relationships in acid–base reactions.

Buffering Regions, Endpoints, and Indicators

The pH curves for acid–base reactions have characteristic shapes. You have learned that a common reason for plotting a pH curve is to determine the value of the solution's pH when an acid–base reaction reaches its equivalence point. We can then use this information to select an appropriate indicator—one that will produce an easily seen endpoint when a solution reaches this pH value. Then we can use the same acid–base reaction, done as a titration to that indicator's endpoint, for titration analysis.

In all titration analyses, the critical measured quantity is the titrant volume required to reach the titration endpoint. For accurate analysis, this value needs to be as close as possible to the theoretically exact value needed to reach the reaction equivalence point. Analysis titrations, like all empirical work, necessarily involve some uncertainty. We call any variation between endpoint values and equivalence point values the titration error of an experiment. Good technique and careful application of knowledge can ensure that this variation is as small as possible—preferably negligible.

Remember:

- *Endpoint* refers to that point in a titration analysis where the addition of titrant is stopped. The endpoint is defined (empirically) by the observed colour change of an indicator.
- *Equivalence point* refers to that point in any chemical reaction where chemically equivalent amounts of the reactants have been combined. The equivalence point is defined (theoretically) by the stoichiometric ratio from the reaction equation.

Endpoints are easily detectable because pH changes a great deal, and very abruptly, as the reaction solution changes (at the equivalence point) from a tiny excess of acid to a tiny excess of base (or vice versa). But this effect begs the question: Why, for most of a titration, does the pH hardly change at all?

To better understand the information that a pH curve provides, we will use a familiar reaction about which we already know a great deal. The pH curve for the strong acid–strong base reaction (Figure 2) has three regions of interest. In the course of this excess titration, the pH first changes very slowly, then very rapidly, and finally very slowly again, as titrant is steadily added. Notice that the addition of acid titrant to the base sample initially has very little effect on the pH of the solution in the flask. In fact, the high pH has not changed much even after enough acid has been added to react with 90% of the original amount of the base sample. This nearly level region on a pH curve identifies a buffering region. **Buffering** is the property of some solutions (often called buffer solutions) of resisting (counteracting) any significant change in pH when an acid or a base is added. In this particular case, buffering occurs because any strong acid added immediately reacts with excess hydroxide ions. Consider that before *any* acid is added, the sample solution is primarily water molecules and hydroxide ions.

Learning Tip

When you began to study acids and bases, the term "neutralize" was understood to refer to an acid–base reaction that had the same final pH as neutral pure water: a pH of 7. Later, you learned that the pH at the equivalence point for an acid–base reaction is almost never 7, except for the strong acid–strong base reaction of hydronium ions with hydroxide ions.

As commonly used, the word "neutralize" is taken to have a more general meaning: that one substance can completely or partially lessen the acidic or basic properties of another substance. When we say sodium carbonate can be used to neutralize spilled nitric acid (**Figure 1**), we mean that adding the base brings the pH value up much closer to neutral.

Figure 1
Soda ash (sodium carbonate) is blown onto nitric acid that has spilled from some railway tank cars, to neutralize the highly reactive and dangerous acid.

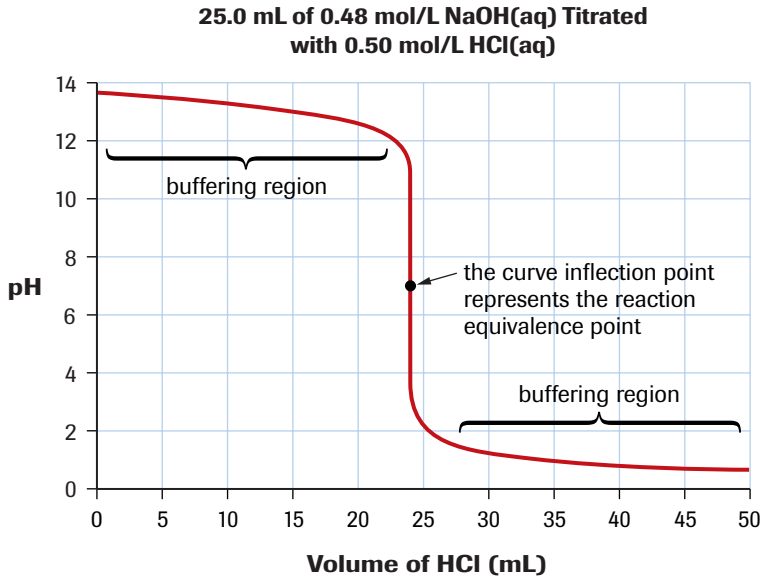


Figure 2
This pH curve for the continuous and excess addition of 0.50 mol/L HCl(aq) to a 25 mL sample of 0.48 mol/L NaOH(aq) helps chemists to understand the nature of acid–base reactions.

Learning Tip

Recall from Unit 4 that the inflection point of any plotted curve is the point where the curvature of the line changes direction. For instance, on the strong acid–strong base pH curve in Figure 2, the line curves downward until about 24 mL of acid has been added. At some observable point, the line curvature changes to upward.

For this specific titration, the change in pH is so large and so rapid that the pH plot becomes a nearly vertical line. In such a case the equivalence point can also be identified as the "mid-point" of the steep drop in the plotted line.

Also recall that, for this particular reaction (only), we already know (from memory) that the equivalence point pH must be 7.0 (at SATP), without actually needing to plot a titration curve: The reaction of hydroxide and hydronium ions is highly quantitative, and the only product is water.

As long as a large amount of hydroxide ions is present, any added acid is immediately converted to water, producing a solution that *still* consists primarily of water molecules and hydroxide ions. The hydroxide ion concentration decreases a little, but that affects the solution pH value only very slightly. This pH "levelling effect" finally fails near the equivalence point—when the hydroxide ions in the solution become almost completely consumed. But, until then, the solution maintains a (nearly) constant pH. This buffering property turns out to be critically important for a great number of reactions in applied chemistry and biology. Note that once *excess* acid has been added, the solution consists primarily of water molecules and hydronium ions. Again, the pH remains stable because adding more hydronium ions now does not change the nature of the solution; it only increases the hydronium ion concentration slightly. Another buffering region is established—this time at a low pH. You will learn more about the causes of buffering regions and the nature of buffer solutions later in this section.

Following the first buffering region there is a very rapid change in pH for a very small additional volume of the titrant. The inflection point on the pH curve represents the equivalence point of this reaction: At this point, we know from theory that the pH must be 7. We also know from experience (Chapter 8) that this reaction can be used for titration analysis, if an indicator is selected that changes colour in solution at a pH very close to 7. As shown in Figure 3, bromothymol blue indicator has a colour change pH range with a middle value *very* close to (just slightly below) pH 7, which makes it an appropriate indicator for this particular reaction. The values below show that the (theoretical) titrant volume required for complete reaction, as predicted by calculation, *should* be 24 mL. Figure 3 shows that if the colour change of bromothymol blue to a green intermediate colour is the endpoint, then the titrant volume *actually* measured at the endpoint (24 mL) is negligibly different from the theoretical predicted value. So, this titration analysis gives very accurate results.

$OH^-(aq)$	+	$H_3O^+(aq)$	$\rightarrow 2\ H_2O(l)$
25 mL × 0.48 mol/L		24 mL × 0.50 mol/L	
12 mmol		12 mmol	

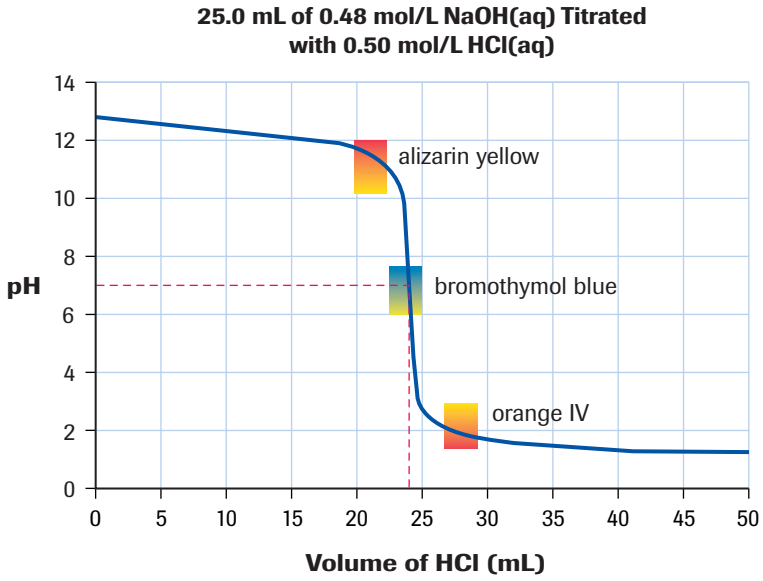


Figure 3
Alizarin yellow is not a suitable indicator because it will change colour long before the equivalence point of this strong acid–strong base reaction, which theoretically has a pH of exactly 7. Orange IV is also unsuitable; its colour change would occur too late. The pH at the middle of the colour change range for bromothymol blue is 6.8, which very closely matches the equivalence point pH; so, a titration analysis endpoint for this reaction, as indicated by bromothymol blue, should give accurate results.

Acid–Base Indicator Equilibrium

Acid–base indicators may be better understood and explained by using Brønsted–Lowry definitions. Any acid–base indicator is really two entities for which we use the same name: a Brønsted–Lowry conjugate acid–base pair. At least one (most often both) of the entities is visibly coloured, so you can tell simply by looking when it forms or is consumed in a reaction. Phenolphthalein is a common example (**Figure 4**), where the conjugate base form is bright red and the conjugate acid form is colourless. Typically, common indicators such as methyl red (**Figure 5**) have quite complex molecular formulas, so we use a (very simplified) shorthand to identify them, for convenience. For example, we symbolize the (invisible) acid form of phenolphthalein as HPh, and the (bright red) base form as Ph^-. When an indicator equilibrium is shifted to the point where equal concentrations of both forms exist, an intermediate colour may be observed. For example, equal concentrations of the blue and yellow forms of bromothymol blue (at a pH of 6.8) appear green to the human eye.

The explanation of the behaviour of acid–base indicators depends, in part, on both the Brønsted–Lowry concept and the equilibrium concept. *An indicator is a conjugate weak acid–weak base pair formed when an indicator dye dissolves in water.* Using HIn(aq) to

Figure 4
Sodium hydroxide solution has been added to hydrochloric acid containing phenolphthalein indicator, which is colourless in acids and red in bases. The red colour, indicating the temporary presence of some unreacted sodium hydroxide, is rapidly disappearing as the flask contents swirl and mix.

Figure 5
A few common acid–base indicators are shown here. Each indicator has its own pH range over which it changes colour from the acid form (HIn) at the lower pH value to the base form (In^-) at the higher pH value. Material Safety Data Sheets are available for these chemicals.

represent the acid form and $In^-(aq)$ to represent the base form of any indicator, we can write the following equilibrium equation. (Litmus colours are given below the equation as an example.)

conjugate pair

$$\underset{\text{acid}}{HIn(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftarrows \underset{\text{base}}{In^-(aq)} + \underset{\text{acid}}{H_3O^+(aq)}$$

red (litmus colour) blue

According to Le Châtelier's principle, an increase in the hydronium ion concentration will shift the equilibrium to the left. Then more indicator will change to the colour of the acid form (HIn(aq)). This change happens, for example, when litmus is added to an acidic solution. Similarly, in basic solutions the hydroxide ions remove hydronium ions by reacting with them to form water, with the result that the equilibrium shifts to the right. Then the base colour of the indicator (In^-) predominates. Since different indicators have different acid strengths, the acidity or pH of the solution at which an indicator changes colour varies (**Figures 5** and **6**). These pH values have been measured and are reported in the table of acid–base indicators on the inside back cover of this book.

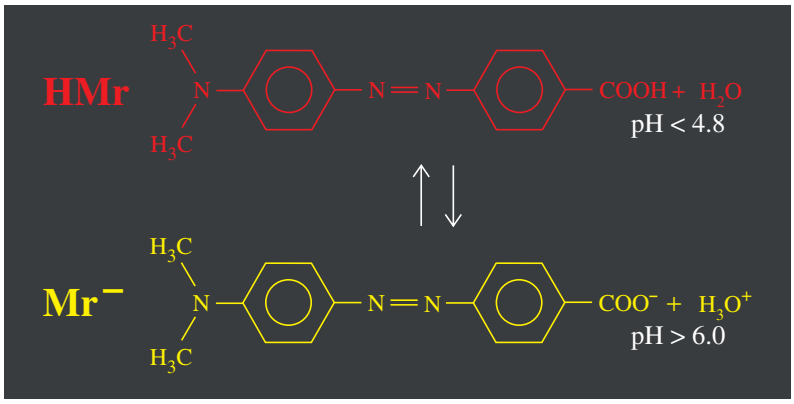


Figure 6
The visible colour of methyl red indicator depends on the equilibrium proportions of its two coloured forms at the pH of the solution in which it is placed. Methyl red exists predominantly in its red (acid) form at pH values less than 4.8, and in its yellow (base) form at pH values greater than 6.0. Between pH values of 4.8 and 6.0, intermediate orange colours occur, as both forms of the indicator are present in detectable quantities.

Learning Tip

Typically, acid–base indicators such as methyl red (**Figure 6**) are large molecules with quite complex formulas. Smaller molecules and ions are less likely to interact with light waves in the visible spectrum.

The shorthand symbolism we use to represent indicators is partly for convenience, but also partly to reinforce the concept that indicators are conjugate acid–base pairs. Consider the actual formulas for the methyl red entities, which we represent as HMr for the acid form, and Mr^- for the base form. This simplified symbolism makes the proton transfer, which causes the colour change, more obvious.

Practice

1. The shape of a pH curve is interpreted to describe the change of properties throughout the course of an acid–base reaction.
(a) In terms of curve shape, describe the characteristics of a buffering region.
(b) In terms of pH change and titrant volume, explain what a buffering region represents.
(c) In terms of curve shape, describe the characteristics near an equivalence point.
(d) In terms of pH change and titrant volume, explain what an equivalence point represents.

Use this information to answer questions 2 to 4.

According to the Brønsted–Lowry concept, acid–base indicators are simply coloured conjugate acid–base pairs. As for all other weak acids, the conjugate acid forms of these indicators must differ in strength for different entities.

2. For each indicator following, write a Brønsted–Lowry equilibrium equation for the reaction of the acid form of the indicator with water, to form a hydronium ion and the

base form of the indicator. Use the same indicator symbolism as used in the table of Acid–Base Indicators on the inside back cover of this book. Identify both conjugate acid–base pairs for each equation, and label all entities "acid" or "base."
(a) methyl orange
(b) indigo carmine
(c) thymol blue (the entity with two "H's" in the symbolized formula)
(d) thymol blue (the entity with one "H" in the symbolized formula)
(e) bromothymol blue

3. Which indicator entity, in your answers to question 2, can behave as both an acid and a base? What chemical term is used to describe this property of an entity?

4. (a) Refer to the table of Acid–Base Indicators to determine which of the five conjugate acid forms for the indicators in question 2 is the strongest acid. (Note the colour change pH ranges.) Then rank the other four indicators beneath it in order of decreasing strength, as in a relative strengths of acids table.
(b) Suppose that five identical samples of an aqueous hydroxide ion solution each have four drops of a different indicator (from question 2) added. If each sample is now titrated with the same HCl(aq) titrant, in which indicator/sample combination will the least amount of titrant cause a colour change?

Polyprotic Entities and Sequential Reactions

Expanding on what you learned in Chapter 8, and adding the Brønsted–Lowry concept, we now examine some acids and bases that can lose (or gain) more than one proton. Polyprotic acids can lose more than one proton, and polyprotic bases can gain more than one proton, in Brønsted–Lowry transfers. If more than one proton transfer actually occurs in the course of a titration, chemists believe the process occurs as a series of single-proton transfer reactions. Typical pH curves for reactions of diprotic or triprotic acids and bases differ from those of monoprotic acids and bases—and can provide useful information about the reactions going on.

We observe (**Figure 7**) that the pH curve for the addition of HCl(aq) to Na_2CO_3(aq) shows two equivalence points—two significant changes in pH. Chemists interpret such curves as indicating how many quantitative reactions have occurred, sequentially, for that particular acid–base titration. Here, for example, two successive quantitative reactions have occurred. The two equivalence points evident in Figure 7 can be explained by two different proton transfer equations.

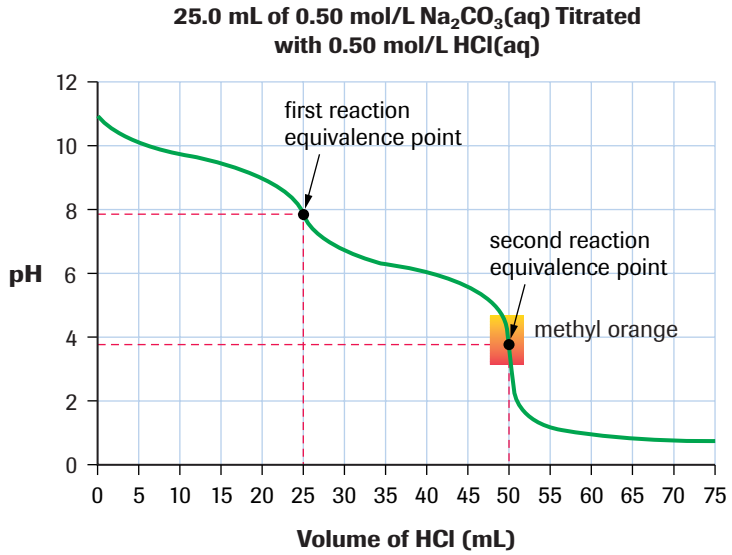
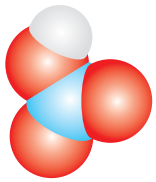
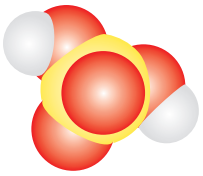


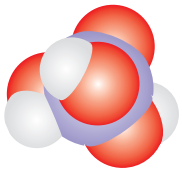
Figure 7
A pH curve for the addition of 0.50 mol/L HCl(aq) to a 25.0 mL sample of 0.50 mol/L Na_2CO_3(aq) can be used to select an appropriate indicator for this reaction done as a titration analysis. The colour change of methyl orange (from pH 4.4 to pH 3.2) means it will show an endpoint that corresponds closely to the second reaction equivalence point.



nitric acid, $HNO_3(aq)$



sulfuric acid, $H_2SO_4(aq)$



phosphoric acid, $H_3PO_4(aq)$

Figure 8

For oxyacids, the protons that transfer in Brønsted–Lowry reactions are covalently bonded to oxygen atoms (identified by a red colour in the models above). Of these three examples, the monoprotic and diprotic acids are strong acids, and the triprotic acid is a weak acid.

Acid formulas were originally derived from stoichiometric evidence. Arguably, it would be more informative to write the molecular formulas differently, as NO_2OH, $SO_2(OH)_2$, and $PO(OH)_3$, to clarify the bonding concept. In both science and society, however, once conventions are established, they are difficult to change.

First, protons transfer from hydronium ions to carbonate ions, the strongest base present in the initial sample. The first significant drop in pH is evidence that the first reaction is quantitative. We write the Brønsted–Lowry equation in the usual way, starting with the acid and base entities present in the sample solution, and also listing the $H_3O^+(aq)$ that is being added.

$$\overset{SA}{H_3O^+(aq)}, Cl^-(aq), Na^+(aq), \underset{SB}{CO_3^{2-}(aq)}, \overset{A}{\underset{B}{H_2O(l)}}$$

$$H_3O^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + HCO_3^-(aq)$$

Because the first reaction is quantitative, essentially all the carbonate ions will have been consumed at the equivalence point, and an equal quantity of (new) hydrogen carbonate ions will have been formed. Then, in a second reaction, protons transfer from additional (continually added) hydronium ions to the hydrogen carbonate ions that were formed in the first reaction.

$$\overset{SA}{H_3O^+(aq)}, Cl^-(aq), Na^+(aq), \underset{B}{\overset{A}{H_2O(l)}}, \underset{SB}{\overset{A}{HCO_3^-(aq)}}$$

$$H_3O^+(aq) + HCO_3^-(aq) \rightarrow H_2O(l) + H_2CO_3(aq)$$

Because the second reaction is also quantitative, all of the hydrogen carbonate ions have reacted at the equivalence point, and only newly formed carbonic acid molecules remain in the solution. Continuing to add more hydronium ion after this point will cause no significant further change (no third reaction), because the strongest base in the system now is water.

The carbonate ion is a *diprotic base* because it can accept a total of two protons. Other polyprotic bases include sulfide ions and phosphate ions. The conjugate entities formed when these bases gain successive protons are:

$$S^{2-}(aq) \text{ — } HS^-(aq) \text{ — } H_2S(aq)$$

$$PO_4^{3-}(aq) \text{ — } HPO_4^{2-}(aq) \text{ — } H_2PO_4^-(aq) \text{ — } H_3PO_4(aq)$$

Other polyprotic acids include oxalic acid and phosphoric acid (**Figure 8**).

$$HOOCCOOH(aq) \text{ — } HOOCCOO^-(aq) \text{ — } OOCCOO^{2-}(aq)$$

$$H_3PO_4(aq) \text{ — } H_2PO_4^-(aq) \text{ — } HPO_4^{2-}(aq) \text{ — } PO_4^{3-}(aq)$$

Evidence from pH measurements clearly shows that, for every proton transferred by a polyprotic entity, the strength of the new acid or base entity formed *greatly* decreases. The new entity may be anywhere from 100 to 100 000 times weaker! Chemists believe that electric charge and electrostatic attraction explain this effect. For example, it should logically be much easier to pull a *positively charged* proton away from a *neutral* oxalic acid molecule, than it is to pull one away from a *negatively charged* hydrogen oxalate ion.

Figure 9 shows the pH curve for phosphoric acid titrated with sodium hydroxide. Phosphoric acid is triprotic, so three reactions should be possible. However, note that only two equivalence points are evident. We describe the process as before. At the first equivalence point (pH 4), equal chemical amounts of $H_3PO_4(aq)$ and $OH^-(aq)$ have been combined in solution. As the last of the $H_3PO_4(aq)$ reacts, the pH rises abruptly, because when the reaction moves past the equivalence point, only newly formed $H_2PO_4^-(aq)$ is now present, and it is a much weaker acid than $H_3PO_4(aq)$.

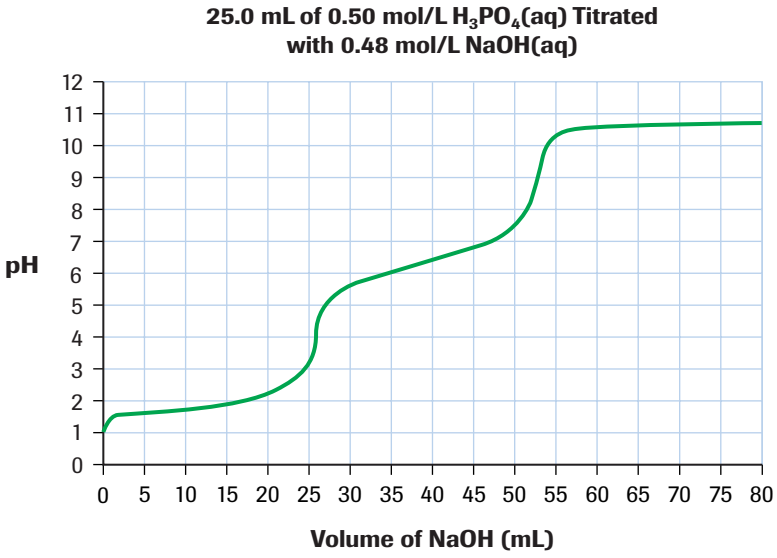


Figure 9
A pH curve for the addition of NaOH(aq) to a sample of H_3PO_4(aq) displays only two rapid changes in pH. This result is interpreted as indicating that there are only two quantitative proton transfer reactions of phosphoric acid with hydroxide ions. The third proton transfer reaction never goes to completion, but instead establishes an equilibrium.

To write the reaction for the transfer of the first proton, start by listing the entities.

$$\underset{SB}{OH^-}(aq), \overset{SA}{H_3PO_4}(aq), \underset{B}{\overset{A}{H_2O}}(l)$$

$$OH^-(aq) + H_3PO_4(aq) \rightarrow H_2O(l) + H_2PO_4^-(aq)$$

Since all the H_3PO_4(aq) has reacted when the reaction has passed the first equivalence point, the second plateau must represent the reaction of OH^-(aq) with $H_2PO_4^-$(aq). The second equivalence point (pH 9) corresponds to the completion of the reaction of $H_2PO_4^-$(aq) with additional OH^-(aq) solution. As the last of the $H_2PO_4^-$(aq) reacts, the pH begins to rise abruptly again because, when the reaction has passed this (second) equivalence point, only newly formed HPO_4^{2-}(aq) is left, and it is an even weaker acid.

$$\underset{SB}{OH^-}(aq), \underset{B}{\overset{A}{H_2O}}(l), \underset{B}{\overset{SA}{H_2PO_4^-}}(aq)$$

$$OH^-(aq) + H_2PO_4^-(aq) \rightarrow H_2O(l) + HPO_4^{2-}(aq)$$

No pH endpoint is apparent for the possible reaction of HPO_4^{2-}(aq) with additional OH^-(aq). A clue to this lack of a third endpoint can be obtained from the table of acids and bases. The hydrogen phosphate ion is an extremely weak acid and apparently does not quantitatively lose protons to OH^-(aq). For the third reaction, an equilibrium is established that gradually shifts right as more base is added. There is no pH increase at a third equivalence point because the reaction never goes to completion.

$$\underset{SB}{OH^-}(aq), \underset{B}{\overset{A}{H_2O}}(l), \underset{B}{\overset{SA}{HPO_4^{2-}}}(aq)$$

$$HPO_4^{2-}(aq) + OH^-(aq) \overset{>50\%}{\rightleftarrows} PO_4^{3-}(aq) + H_2O(l)$$

As a general rule, *only quantitative reactions produce detectable equivalence points in an acid–base titration.*

Learning Tip

When any weak polyprotic acid or base is initially dissolved in water, we always assume that the ionization equilibrium only involves the first proton transfer—to or from water. This is essentially true because the tendency of any entity that is formed by a first ionization to lose or gain a (second) proton is very much less than that of the original polyprotic entity dissolved; so much so that it can safely be considered negligible.

DID YOU KNOW ?

Sulfuric Acid

Sulfuric acid (**Figure 10**) is probably the world's most important industrial chemical. It is used for so many things that the industrial development and standard of living of a country may be thought of as being proportional to its sulfuric acid production. Canada produces approximately four million tonnes every year. U.S. production (the world's largest) is about 10 times as much. The main direct consumer use of sulfuric acid is the 4.5 mol/L solution inside every standard car and truck battery.

Sulfuric acid plants (**Figure 11**) can be quite compact, and are assembled from "off-the-shelf" technology. They involve only a few simple reactions, starting with sulfur (in Alberta, mostly extracted from fossil fuels) and oxygen.

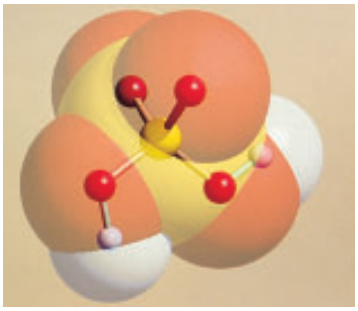


Figure 10
A model of sulfuric acid, showing relative atom size, bonding, and molecular shape

Figure 11
More sulfuric acid is manufactured in North America than any other chemical.

Sulfuric acid, $H_2SO_4(aq)$, is a unique polyprotic acid because it is the only common one for which the first proton loss is already quantitative in aqueous solution; that is, it is the only strong acid that is polyprotic. Sulfuric acid acts like any of the other five common strong acids, except that its 100% ionization produces hydrogen sulfate ions, $HSO_4^-(aq)$, along with hydronium ions, $H_3O^+(aq)$. Recall that of all the anions of this type (like $HCO_3^-(aq)$, or $HPO_4^{2-}(aq)$), the hydrogen sulfate ion is the only one that is a weaker base than water, so it cannot react as a base in aqueous solution. When reacting as an acid, however, hydrogen sulfate ion is one of the stronger weak acids, and usually reacts quantitatively with bases (except for very weak bases, of course). So sulfuric acid will usually, but not always, react with a base (assuming the base is in excess) in two complete proton transfer reactions, one after the other. When you first began a study of reactions of acids and bases, you would have written a complete reaction of sulfuric acid with sodium hydroxide as

$$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

This reaction equation, if you think about it now, implies that you assumed that both of this acid's "hydrogens" (protons) were "replaced" (transferred). You had no information at that time, however, about how this transfer occurs. For simple stoichiometric calculations based on this reaction, this limited understanding (and simplified equation) worked perfectly well. Explaining and predicting other reactions of sulfuric acid, however, is a different story. To do so, understanding how the neutralization process occurs (as two distinct and sequential reactions) is necessary, because both reactions may not be quantitative when a different (weaker) base is involved, and stoichiometric calculation can only be done for a reaction that is quantitative.

There are almost no overall reactions of common polyprotic acids or bases that have more than two definite endpoints. For any such reactions that are actually done as analysis titrations, an indicator can be selected so that the titration can be stopped at either chosen equivalence point. For the titration of sodium carbonate solution with hydrochloric acid, this would mean titrating through two sequential quantitative reactions to the second equivalence point, as shown in Figure 7. For this titration, the second equivalence point involves a greater pH change, and thus is easier to detect (more accurate). As we found earlier, methyl orange indictor is suitable for detecting this second equivalence point.

For purposes of stoichiometric calculation, we can combine sequential quantitative Brønsted–Lowry reaction equations into a single "overall" reaction equation. This example is for the titration of sodium carbonate solution with hydrochloric acid.

1. $H_3O^+(aq) + CO_3^{2-}(aq) \rightarrow \cancel{HCO_3^-(aq)} + H_2O(l)$ followed by
2. $H_3O^+(aq) + \cancel{HCO_3^-(aq)} \rightarrow H_2CO_3(aq) + H_2O(l)$ "totals" to

$$2\ H_3O^+(aq) + CO_3^{2-}(aq) \rightarrow H_2CO_3 + 2\ H_2O(l) \quad \text{(overall reaction)}$$

For purposes of stoichiometric calculation, this equation is equivalent to writing

$$2\ HCl(aq) + Na_2CO_3(aq) \rightarrow H_2CO_3(aq) + 2\ NaCl(aq)$$

because, either way, the reactant acid–base stoichiometric ratio is found to be 2:1. Chemists normally use the simplest representation that will be useful, so Brønsted–Lowry equations are more often used for correctly predicting products and equilibria, whereas standard chemical formula equations are more often used for "doing" stoichiometry as, for example, in titration analyses.

SUMMARY pH Curve Reaction Information

Empirical pH curves provide a wealth of information:

- initial pH of sample solutions
- pH when excess titrant is added
- number of quantitative reactions
- non-quantitative (equilibrium) reactions
- equivalence point(s) for indicator selection
- buffering regions

Practice

5. How is buffering action displayed on a pH curve?

6. How are quantitative reactions displayed on a pH curve?

7. How is a pH curve used to choose an indicator for a titration?

8. An acetic acid sample is titrated with sodium hydroxide (**Figure 12**.)

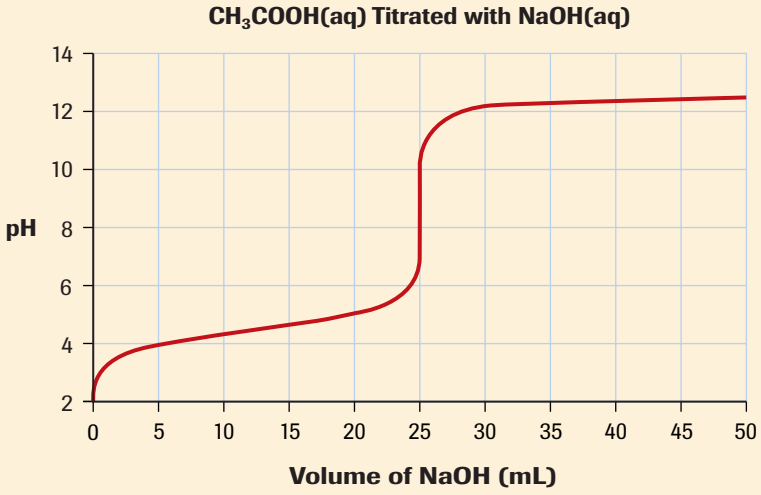


Figure 12
The pH curve for the addition of 0.48 mol/L NaOH(aq) to 25.0 mL of 0.49 mol/L $CH_3COOH(aq)$ illustrates pH changes during the reaction of a weak acid with a strong base.

(a) Based on Figure 12, estimate the pH at the equivalence point.
(b) Choose an appropriate indicator for this titration.
(c) Write a Brønsted–Lowry equation for this reaction.
(d) At the very beginning of the titration, before the curve levels off, it rises. Explain this rise in terms of entities present in the mixture before and after beginning the titration.

9. A sodium phosphate solution is titrated with hydrochloric acid (**Figure 13** on next page).
(a) Why are only two equivalence points evident?
(b) Write three Brønsted–Lowry equations for the sequential reactions shown on the pH curve in Figure 13. Communicate the position of equilibrium for each of the three reactions.

10. Oxalic acid reacts quantitatively in a two-step overall reaction with a sodium hydroxide solution. Assuming that an excess of sodium hydroxide is added, sketch a pH curve (without any numbers) for all possible reactions.

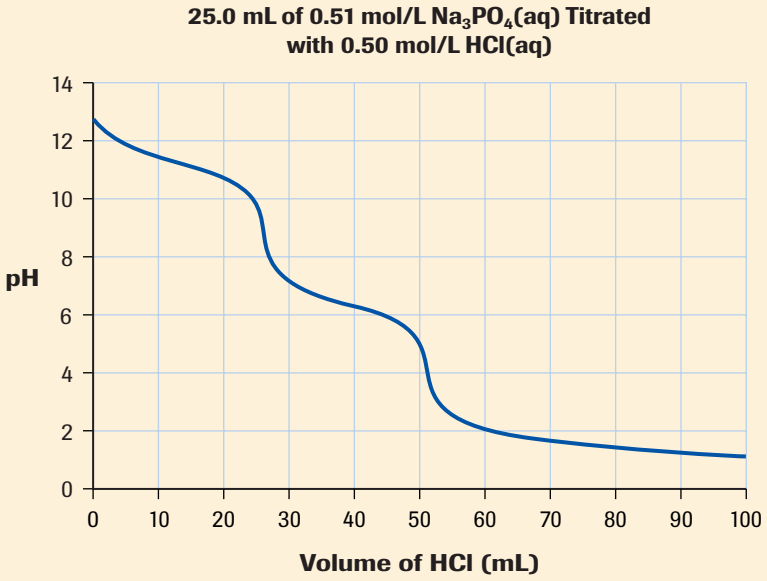


Figure 13
The pH curve for the addition of HCl(aq) to Na_3PO_4(aq) can be interpreted using the Brønsted–Lowry acid–base concept.

pH Curve Shape versus Acid and Base Strength

You have learned that the reaction of the strongest possible acid in aqueous solution, $H_3O^+(aq)$, and the strongest possible base in aqueous solution, $OH^-(aq)$, is quantitative, and always results in an equivalence point pH of 7.00 at 25 °C. Not all titrations involve the hydronium and the hydroxide ions, however.

pH curves show that some weak acids (such as acetic acid) react quantitatively with $OH^-(aq)$ (**Figure 12**). The reactions of some weak bases (such as $PO_4^{3-}(aq)$ and $HPO_4^{2-}(aq)$) with $H_3O^+(aq)$, can also produce a quantitative reaction (**Figure 13**). The strongest of the weak acids also react quantitatively with the strongest of the weak bases. For example, the reaction of $HSO_4^-(aq)$ with $CO_3^{2-}(aq)$ is a quantitative reaction. The farther apart the reacting acid and base are on the Relative Strengths of Aqueous Acids and Bases table (i.e., the larger the difference in K_a), the more likely it is that the reaction will be quantitative. After plotting many pH curves, chemists have developed the general pH curve reference diagram shown in **Figure 14**.

Learning Tip

Recall that, for the examples you have studied, bromothymol blue has been an appropriate indicator for the SA–SB reaction, because it detects an endpoint with a pH of 7 very well. Methyl orange detects endpoint pH values around 4 well, and is, therefore, useful for many SA–WB reactions. Finally, phenolphthalein detects endpoints with pH values around 10 well, and is, therefore, useful for many WA–SB titrations.

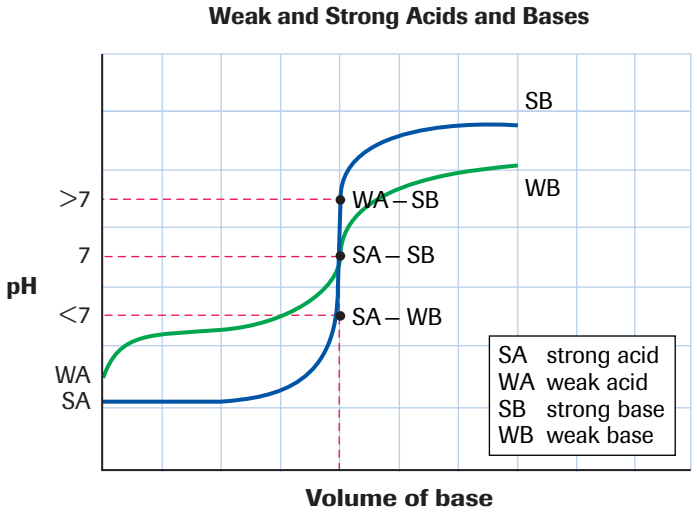


Figure 14
Laboratory evidence is generalized here to show approximations of the pH curves for quantitative reactions of weak and strong acids and bases. Note the initial change in pH for curves involving "weak" entities, due to the immediate change of the kinds of entities present in solution when the titration begins.

The (stoichiometric) equivalence point pH for a strong acid–strong base (SA–SB) reaction is seven (7). The equivalence point pH of any quantitative strong acid–weak base (SA–WB) reaction is less than seven (<7), whereas that of any quantitative weak acid–strong base reaction (WA–SB) is greater than seven (>7).

The composite curves in Figure 14 are not acceptable (do not predict well) for any reactions between a weak acid and a weak base. Weak acid–weak base reactions often do not *have* a detectable equivalence point because they are usually not quantitative. For all intents and purposes, analysis reactions and stoichiometric calculations are not done for weak acid–weak base reactions, so a pH curve for such a reaction is simply irrelevant.

The pH of a solution at the equivalence point of an acid–base reaction may be explained by considering the nature of those entities that are present in significant quantities at that point. The entities present at an equivalence point can be predicted either by following the five-step Brønsted–Lowry method, or simply by converting a chemical substance formula equation into a net ionic equation.

Now let's examine a case of each of the common acid–base reaction types, and explain the equivalence point pH in each case. Each of the examples used is a quantitative reaction.

Strong Acid–Strong Base Reaction

For example, nitric acid reacts with potassium hydroxide: SA–SB pH = 7.

$$\overset{SA}{H_3O^+(aq)}, NO_3^-(aq), K^+(aq), \overset{SB}{OH^-(aq)}, \overset{A}{H_2O(l)}\ \overset{B}{}$$

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)$$

or

$$HNO_3(aq) + KOH(aq) \rightarrow H_2O(l) + KNO_3(aq)$$

$$H^+(aq) + \cancel{NO_3^-(aq)} + \cancel{K^+(aq)} + OH^-(aq) \rightarrow H_2O(l) + \cancel{K^+(aq)} + \cancel{NO_3^-(aq)}$$

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

At the equivalence point, water is the only acid or base entity present, which produces a neutral solution (pH = 7).

Strong Acid–Weak Base Reaction

For example, hydrochloric acid reacts with aqueous ammonia: SA–WB pH < 7.

$$\overset{SA}{H_3O^+(aq)}, Cl^-(aq), \overset{SB}{NH_3(aq)}, \overset{A}{H_2O(l)}\ \overset{B}{}$$

$$H_3O^+(aq) + NH_3(aq) \rightarrow H_2O(l) + NH_4^+(aq)$$

or

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

$$H^+(aq) + \cancel{Cl^-(aq)} + NH_3(aq) \rightarrow NH_4^+(aq) + \cancel{Cl^-(aq)}$$

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$$

At the equivalence point, the only acid or base entity present (other than water) is the ammonium ion, which is a weak acid, resulting in an acidic solution (pH <7).

Learning Tip

Recall that entities common to both sides of the equation are cancelled out and the coefficients of the remaining entities are reduced to the simplest ratio, in a net ionic equation.

Weak Acid–Strong Base Reaction

For example, acetic acid reacts with barium hydroxide: WA–SB pH > 7.

$$\overset{SA}{CH_3COOH(aq)}, Ba^{2+}(aq), \overset{SB}{OH^-(aq)}, \overset{A}{\underset{B}{H_2O(l)}}$$

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

or

$$2\,CH_3COOH(aq) + Ba(OH)_2(aq) \rightarrow 2\,H_2O(l) + Ba(CH_3COO)_2(aq)$$

$$2\,CH_3COOH(aq) + \cancel{Ba^{2+}(aq)} + 2\,OH^-(aq) \rightarrow 2\,H_2O(l) + \cancel{Ba^{2+}(aq)} + 2\,CH_3COO^-(aq)$$

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

At the equivalence point, the only acid or base entity present (other than water) is the acetate ion, which is a weak base, resulting in a basic solution (pH >7).

Learning Tip

In an equation for a titration, a single arrow, ⟶, is used. The reaction represented by the equation must be quantitative in order for any stoichiometric calculations based on the equation to be valid. In such cases, chemical formula equations are often the most convenient form.

SUMMARY Titration Generalizations

- Strong acid–strong base reactions are quantitative (100%) and have an equivalence point pH = 7.
- Strong acid–weak base quantitative reaction equivalence points have a pH <7.
- Weak acid–strong base quantitative reaction equivalence points have a pH >7.
- Polyprotic entity samples produce sequential reactions in titrations, each of which may or may not be quantitative.

WWW WEB Activity

Simulation—Titration of Polyprotic Acids and Bases

These two simulations enable you to explore the pH curves that result from various titrations. Of course, polyprotic acids and bases each have more than one *K* value, so the shapes of their titration curves will reflect this. Predict the shapes of the curves before working through the exercises.

www.science.nelson.com GO

Practice

11. For the first quantitative reaction in each of the following acid–base titrations, predict (where possible) whether the equivalence point pH will be greater than, less than, or equal to 7.

(a) hydroiodic acid + aqueous sodium hydrogen phosphate ⟶
(b) boric acid + aqueous sodium hydroxide ⟶
(c) aqueous sodium hydrogen sulfate + aqueous potassium hydroxide ⟶
(d) hydrochloric acid + solid magnesium hydroxide ⟶
(e) hydrosulfuric acid + aqueous sodium hydrogen carbonate ⟶
(f) sulfuric acid + aqueous ammonia ⟶

12. Assume only three indicator solutions are available in your lab: methyl orange, bromothymol blue, and phenolphthalein. Choose the most suitable indicator for detecting the equivalence point of each of the following acid–base titrations (for the first quantitative reaction only).
(a) $HBr(aq) + Ca(OH)_2(s) \longrightarrow$
(b) $HNO_3(aq) + Na_2CO_3(aq) \longrightarrow$
(c) $KOH(aq) + HNO_2(aq) \longrightarrow$

13. The following formulas each represent a solution at an acid–base reaction equivalence point. From the entities present in each solution, predict the observed pH as being greater than, less than, or equal to 7.
(a) $NH_4Cl(aq)$
(b) $Na_2S(aq)$
(c) $KNO_3(aq)$
(d) $NaHSO_4(aq)$

14. Use the five-step Brønsted–Lowry method to predict the overall reaction net ionic equation when the following chemicals are mixed.
(a) solutions of perchloric acid and sodium carbonate (A pH curve shows two protons are transferred quantitatively in successive reactions.)
(b) solutions of nitrous acid and potassium hydroxide
(c) solutions of phosphoric acid and sodium hydroxide (A pH curve shows two protons are transferred quantitatively in successive reactions.)

15. Write a standard chemical formula equation, and also the net ionic equation, for the predominant reaction that occurs when each of the following pairs of reagents mix.
(a) Stomach acid is neutralized by solid magnesium hydroxide.
(b) Aqueous ammonia is added to sulfurous acid.
(c) A solution of sulfuric acid is neutralized by sodium hydroxide. (A pH curve indicates two quantitative reactions.)

pH Curve Buffering Regions and Buffer Solutions

A titration pH curve for any quantitative acid–base reaction shows at least one region where buffering action occurs between the beginning of the titration and the equivalence point. If the titration is continued much past the equivalence point, it enters another region of buffering. Such a region represents a solution in which partial reaction has occurred, and, therefore, contains significant amounts of both entities of a conjugate acid–base pair. The term **buffer** refers specifically to the combination of any weak acid with its conjugate base, in the same solution. Buffer solutions have a specific pH due to the nature and concentration of the entities present, and change pH very little when other acids or bases are added—provided that the quantity added is much less than the quantities of the conjugate pair entities present in the buffer.

For example, consider the titration of acetic acid with sodium hydroxide (**Figure 15**). The solution pH is approximately 4.8 when 10 mL of sodium hydroxide solution has been added. This volume represents one-half of the (calculated) equivalence point volume of titrant. At this point in the reaction, one-half of the acetic acid originally present will have reacted (changed to acetate ions), according to the following equation:

$$OH^-(aq) + CH_3COOH(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

The mixture, therefore, now contains approximately equal amounts of the remaining unreacted weak acid, CH_3COOH, and of the conjugate base, CH_3COO^-, produced in the reaction. Chemists would describe this mixture as an acetic acid–acetate ion buffer.

Learning Tip

You have observed (Figure 2, page 752) that the strong acid–strong base reaction pH curve shows that the conjugate pair $H_3O^+(aq)$–$H_2O(l)$ will maintain a stable (very low) pH; and that the $H_2O(l)$–$OH^-(aq)$ pair will stabilize pH at a very high value.

Even though these solutions certainly do produce a buffering effect, they are not technically considered to be buffers, because in each case one of the two conjugate pair entities (water) is also the solution solvent, and is present in great excess.

A buffer is normally thought of as an aqueous solution mixture of a weak acid and its conjugate base, with both entities of the conjugate pair present in significant quantity, but with both quantities much less than the quantity of the solution solvent (water) present.

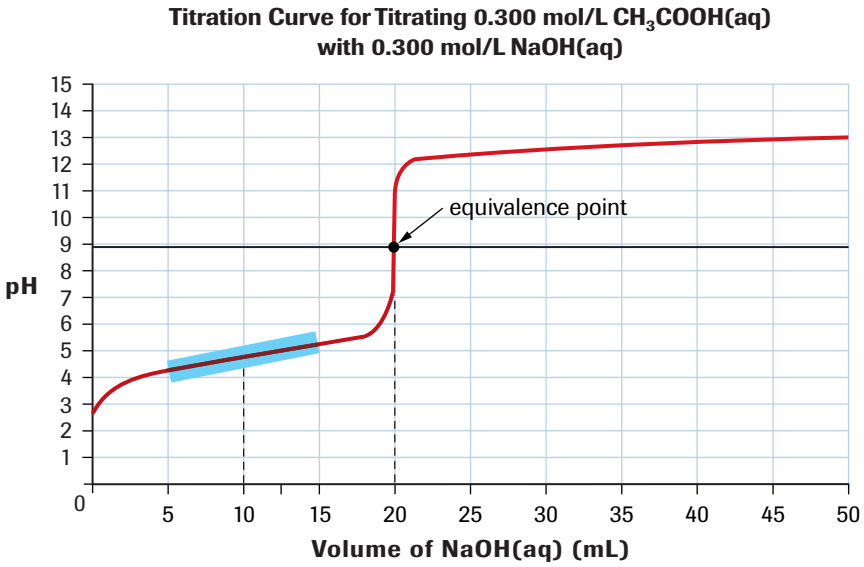


Figure 15
The highlighted plateau shows an effective buffering region during this titration of aqueous acetic acid with sodium hydroxide. At the point halfway to the equivalence point, the solution is a 1:1 ratio mix of an acetic acid–acetate ion buffer.

Learning Tip

Buffers are normally prepared as mixtures of a weak acid with a solution of some salt of that weak acid. Thus, dissolving solid sodium acetate in a solution of acetic acid would produce a buffer solution with properties the same as those of the highlighted buffering region of Figure 15.

Buffering can be readily explained using Brønsted–Lowry equations. Suppose a small amount of NaOH(aq) is added to the acetic acid–acetate ion buffer. Using the five-step method for predicting the predominant acid–base reaction (page 731), the following equation is obtained:

$$\overset{\text{SB}}{Na^+(aq)}, \overset{\text{SB}}{OH^-(aq)}, \overset{\text{SA}}{CH_3COOH(aq)}, \overset{\text{B}}{CH_3COO^-(aq)}, \overset{\text{B}}{H_2O(l)}$$

$$OH^-(aq) + CH_3COOH(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

Figure 15 shows that this reaction is quantitative. A small amount of OH^- would convert a small amount of acetic acid to acetate ions. The overall effect will be just a small decrease in the ratio of acetic acid to acetate ions in the buffer and a slight increase in the pH. The very small change in concentration of each entity of the acid–base conjugate pair present, and the complete consumption of the added hydroxide ions in the process, explains why the pH change is small. This buffer would work equally well if a small amount of a strong acid, such as HCl(aq), were to be added. Evidence indicates that the reaction that occurs in that case is also quantitative.

$$\overset{\text{SA}}{H_3O^+(aq)}, \overset{\text{SB}}{Cl^-(aq)}, \overset{\text{A}}{CH_3COOH(aq)}, \overset{\text{B}}{CH_3COO^-(aq)}, \overset{\text{B}}{H_2O(l)}$$

$$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow H_2O(l) + CH_3COOH(aq)$$

Added hydronium ion is consumed and the mixture then has a slightly higher ratio of acetic acid to acetate ions and a slightly lower pH. **Figure 16** illustrates the concept of **buffer capacity**—the limit of the ability of a buffer to maintain a pH level. When the entity of the conjugate acid–base pair that reacts with an added reagent is completely consumed, the buffering fails and the pH changes dramatically.

The ability of buffers to maintain a relatively constant pH is important in many biological processes where certain chemical reactions can only occur at a specific pH value. Many aspects of cell functions and metabolism in living organisms are very sensitive to pH changes. For example, each enzyme carries out its function optimally over a small pH range. One essential buffer operates to maintain a stabilized pH in the internal fluid of all living cells. This critically important buffer is a mixture of dihydrogen phosphate ions and hydrogen phosphate ions. In mammals, cellular fluid has a pH in the range

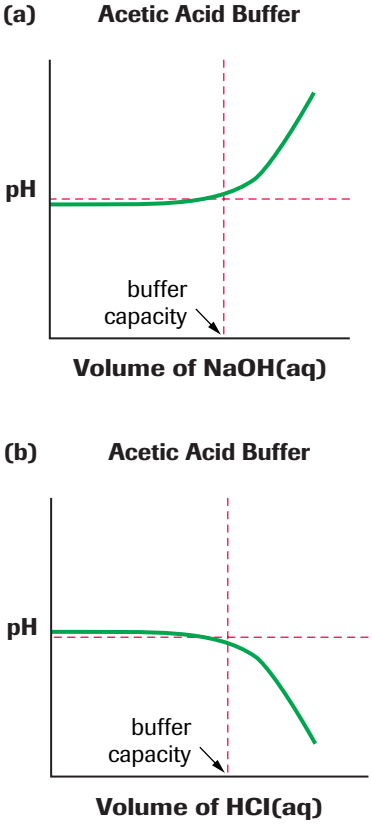


Figure 16
When an initial chemical amount of a buffer is eventually depleted, the pH then changes very quickly.

of 6.9 to 7.4. The $H_2PO_4^-(aq)$–$HPO_4^{2-}(aq)$ buffer system has a pH of 7.2 when the concentrations of these two conjugate entities are equal. With small variations in concentration, this buffer is effective in maintaining optimum pH levels for the innumerable reactions going on within any given cell. The major buffer system in the blood and other body fluids (except the cytoplasm within cells) is the conjugate acid–base pair $H_2CO_3(aq)$–$HCO_3^-(aq)$. Blood plasma has a remarkable buffering ability, as shown by the empirical results in **Table 1**. Since production of the entities of this buffer in the body is a *continuous* process, the buffer is not a limiting reagent, and you do not ordinarily have to worry about using up your buffering capacity.

Table 1 Buffering Action of Neutral Saline Solution and of Blood Plasma

Solution (1.0 L)	Initial pH of mixture	Final pH after adding 1 mL of 10 mol/L HCl
neutral saline	7.0	2.0
blood plasma	7.4	7.2

Human blood plasma normally has a pH of about 7.4. Any change of more than 0.4 pH units, induced by poisoning or disease, can be lethal. If the blood were not buffered, the acid absorbed from a glass of orange juice would probably be fatal.

WEB Activity

Simulation—Preparation of Buffer Solutions

This simulation shows you how to select an appropriate acid–base conjugate pair to make a buffer of the desired pH.

www.science.nelson.com GO

Buffers are also important in many consumer, commercial, and industrial applications. Fermentation and the manufacture of antibiotics require buffering to optimize yields and to avoid undesirable side reactions. The production of various cheeses, yogurt, and sour cream are very dependent on controlling pH levels, since an optimum pH is needed to control the growth of micro-organisms and to allow enzymes to catalyze fermentation processes. Sodium nitrite and vinegar are widely used to preserve food; part of their function is to prevent the fermentation that takes place only at certain pH values.

The *CRC Handbook of Chemistry and Physics* provides recipes for preparing buffer solutions. For example, a buffer with a pH of 10.00 can be prepared by mixing 50 mL of 0.050 mol/L $NaHCO_3(aq)$ with 10.7 mL of 0.10 mol/L $NaOH(aq)$. The reaction to establish the buffer is described in the same way as all other acid–base reactions.

$$\underset{}{Na^+(aq)}, \underset{\text{B}}{\overset{\text{SA}}{HCO_3^-(aq)}}, \underset{\text{SB}}{OH^-(aq)}, \underset{\text{B}}{\overset{\text{A}}{H_2O(l)}}$$

$$HCO_3^-(aq) + OH^-(aq) \rightarrow H_2O(l) + CO_3^{2-}(aq)$$

The buffer preparation recipe reaction converts about $\frac{3}{5}$ of the initial hydrogen carbonate ions into carbonate ions. An aqueous mixture of a 3:2 ratio of these two acid–base conjugates at the concentrations specified has been found empirically to have an equilibrium pH of precisely 10.00 at 25 °C. Buffer mixtures like this one—with highly precise pH values—are routinely used to calibrate pH meters for accuracy.

BIOLOGY CONNECTION

Homeostasis

Many reactions in the human body produce or consume carbonic acid or hydrogen carbonate ions. When one of these entities is depleted in the blood, Le Châtelier's principle comes into effect, and more of that entity is produced by an equilibrium shift to keep everything in balance.

The carbonic acid in solution in blood is really in equilibrium with dissolved carbon dioxide:

$$CO_2(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq)$$

The enzyme carbonic anhydrase acts as a catalyst to allow this equilibrium to establish rapidly, or reestablish quickly, once shifted. It is possible to make your blood temporarily too basic by deliberately breathing heavily for a long time, thereby causing your body to lose too much carbon dioxide. Doctors call this condition respiratory alkalosis.

There are countless equilibrium reactions interconnected in this way in and around living cells. Biologists refer to this interdependent network of reaction equilibria as an example of homeostasis—the condition of automatic continual readjustment of cells, systems, and whole organisms to very specific conditions. Biology courses will tell you a lot more about homeostasis and the factors that affect it.

www.science.nelson.com GO

EXTENSION

The Hydrogen Carbonate Buffer System

The pH of your blood is maintained at a constant level, courtesy of a series of equilibrium reactions, including a buffer system. This extension outlines the reactions, and gives an example of how climbing at high altitude can upset this delicate balance.

www.science.nelson.com GO

Figure 17
Maud Menten (1879–1960)

DID YOU KNOW ?

Commercial Buffers

Buffers are fairly common, commercially. You can buy buffer mixtures to adjust the pH of aquarium water to suit the type of fish you have. Buffer mixes are sold to add to hot tubs to control the pH of the water. Many food recipes mix ingredients that form natural buffers within the dough, batter, or sauce.

WWW WEB Activity

Canadian Achievers—Maud Menten

Maud Menten (**Figure 17**) was a world-renowned pioneer in explaining the chemical action of enzymes. What key concept was her chief contribution to understanding enzyme activity?

www.science.nelson.com GO

Practice

16. Give both an empirical and a theoretical definition of a buffer.

17. List two buffers that help maintain a normal pH level in your body.

18. Use the five-step method to predict the quantitative reaction of a carbonic acid–hydrogen carbonate ion buffer
(a) when a small amount of HCl(aq) is added
(b) when a small amount of NaOH(aq) is added

19. What happens if a large (excess) amount of a strong acid or base is added to a buffer?

20. Use Le Châtelier's principle to predict what will happen to a benzoic acid–benzoate ion buffer when a small amount of each of the following substances is added:
(a) HCl(aq) (b) NaOH(aq)

21. Which of the following solution pairs, when mixed in equal quantities, will not form an effective buffer?
(a) $HNO_3(aq)$ and $NaNO_3(aq)$
(b) $C_6H_5COOH(aq)$ and $NaC_6H_5COO(aq)$
(c) $NH_3(aq)$ and $NH_4Cl(aq)$
(d) HCl(aq) and NaOH(aq)

INVESTIGATION 16.3 *Introduction*

Testing a Buffer Effect

References provide "recipes" for preparing standard buffer solutions of any desired pH from 1.0 to 13.0. The one used in this investigation has a pH of precisely 7.0, and might be used to calibrate a pH meter, for example. If our theory of buffers is correct, this solution should resist significant change in pH upon gradual addition of outside acid or base entities. Write the Design, Materials, and table of evidence to match the Procedure that is provided. The buffer is prepared by a reaction communicated by the following chemical equation:

$$\underset{\text{excess (acid part of buffer)}}{H_2PO_4^-(aq)} + \underset{\text{limiting reagent}}{OH^-(aq)} \longrightarrow \underset{\text{(base part of buffer)}}{HPO_4^{2-}(aq)} + H_2O(l)$$

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	● Materials	● Evaluation (1, 2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Purpose

The purpose of this investigation is to test our concept of buffers.

Problem

How does the pH change when a strong acid and a strong base are slowly added separately to an $H_2PO_4^-(aq)$–$HPO_4^{2-}(aq)$ buffer?

To perform this investigation, turn to page 769.

CAREER CONNECTION

Microbiologist

Microbiologists study, test for, and isolate microorganisms such as bacteria, fungi, and viruses. As part of a medical or research team, their work is essential for public health and safety.

www.science.nelson.com GO

SUMMARY Brønsted–Lowry Is a Unifying Concept

The five-step Brønsted–Lowry method to explain and predict acid–base reactions is a preferred, acceptable method because it works for all quantitative and non-quantitative reactions studied so far:

- neutralization reactions
- indicator reactions
- buffer reactions
- polyprotic reactions
- excess reactions
- titration reactions

Section 16.4 Questions

1. Draw a pH curve to illustrate the following information about acid–base reaction systems.
   (a) What is buffering?
   (b) Where does buffering appear on a pH curve?
   (c) How are quantitative reactions represented on a pH curve?
   (d) Define endpoint and equivalence point.
   (e) How is a suitable indicator chosen for a titration?
   (f) Do non-quantitative reactions have an endpoint? Explain your answer briefly.
2. Sketch and label generalized pH curves on a single set of axes to illustrate the addition of a strong and a weak base to a strong and a weak acid.
3. Sketch a generalized pH curve for the addition of a strong base to a weak acid. Label the approximate equivalence point pH, and suggest an indicator that could be suitable for titration analysis using this reaction.
4. If the pH of a solution is 6.8, what is the colour of each of the following indicators in this solution?
   (a) methyl red
   (b) chlorophenol red
   (c) bromothymol blue
   (d) phenolphthalein
   (e) methyl orange
5. Use **Figure 18** to answer the following questions.
   (a) How many quantitative reactions have occurred?
   (b) Write the chemical equation for each quantitative reaction.
   (c) State the equivalence point pH for each quantitative reaction.
   (d) Choose a suitable indicator to correspond to the equivalence point pH value(s).
   (e) Identify the buffering region(s) and state the chemical formulas for the entities present in each region.

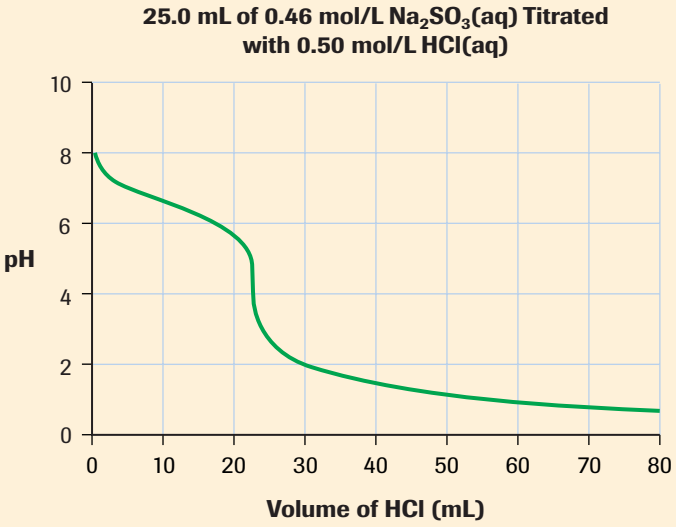


Figure 18
pH curve for the titration of sodium sulfite solution with hydrochloric acid

6. Write a net ionic equation to represent the following acid–base reactions. (Use any method that you find convenient to derive the net ionic equation.)
   (a) Oxalic acid is titrated with aqueous sodium hydroxide. (The indicator detects the second equivalence point.)
   (b) Sodium phosphate is titrated with hydrochloric acid. (The titration is stopped at the first equivalence point.)
   (c) Sodium hydrogen phosphate is titrated with hydrochloric acid. (An indicator is chosen to detect the first equivalence point.)
   (d) Nitric acid is titrated with aqueous barium hydroxide.
   (e) A sulfuric acid spill is neutralized by adding excess lye.
7. Write a formula (non-ionic) equation, and also the corresponding Brønsted–Lowry equation, to represent the following quantitative acid–base reactions.
   (a) Acetic acid is titrated with aqueous sodium hydroxide.
   (b) Nitrous acid is titrated with aqueous barium hydroxide.
   (c) Sodium carbonate is titrated with hydrobromic acid. (The titration is stopped after the first quantitative reaction.)
   (d) Carbonic acid is titrated with aqueous sodium hydroxide. (An indicator endpoint is used to stop the reaction with a stoichiometric ratio of 1:1.)
   (e) A sulfuric acid spill is neutralized by adding excess lye (caustic soda).
8. State two different applications of buffers.
9. Suggest a compound that could be dissolved in a sulfurous acid solution to make an effective buffer.
10. Assume that you have a hydrogen carbonate ion solution. Suggest substances to add to make
    (a) a buffer with a lower pH than the original solution
    (b) a buffer with a higher pH than the original solution
11. Complete the Design of the following investigation report.

Purpose
The purpose of this investigation is to test buffer concepts by quantitatively measuring equilibrium shifts for a buffer system.

Problem
Does the Brønsted–Lowry concept, as applied to buffers, predict changes in equilibrium concentration of $H_3O^+(aq)$ in a standard buffer solution, when strong acids or bases are added?

Materials
pH 7.00 $H_2PO_4^-/HPO_4^{2-}$ buffer solution
pH meter
1.00 mol/L HCl(aq)
1.00 mol/L NaOH(aq)

Extension

12. From a CRC Handbook or any other reference, locate and copy at least one "recipe" for preparing a buffer solution that will have a pH of precisely 5.00 at 25 °C.

INVESTIGATION 16.1

Creating an Acid–Base Strength Table

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	○ Materials	● Evaluation (1)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

An acid–base table organizes common acids (and their conjugate bases) in order of decreasing acid strength (**Figure 1**). Acid strength can be tested several ways, including by a carefully designed use of indicators. Predict the order of strengths using the Relative Strengths of Aqueous Acids and Bases Table (Appendix I). Use the indicators provided to create a valid and efficient Design, in which you clearly identify the relevant variables. Evaluate the Design (only), and suggest improvements if any problems are identified.

Purpose

The purpose of this investigation is to test an experimental design for using indicators to create a table of relative strengths of acids and bases.

Problem

Can the indicators available be used to rank the acids and bases provided in order of strength?

Materials

lab apron
eye protection
0.10 mol/L HCl(aq)
0.10 mol/L $NaHSO_4$(aq)
0.10 mol/L CH_3COOH(aq)
0.10 mol/L $NaHSO_3$(aq)
0.10 mol/L Na_2CO_3(aq)
0.10 mol/L NaOH(aq)
indicators, for example: methyl orange, methyl violet, bromothymol blue, phenolphthalein
(6) 13 × 100 mm test tubes for each indicator or spot plate (microchem)
test-tube rack

Chemicals used include toxic, corrosive, and irritant materials. Avoid eye and skin contact. If you spill any of the chemical solutions on your skin, immediately rinse the area with lots of cool water. In the unlikely situation of getting some of the chemicals in your eye, immediately rinse your eye for at least 15 min and inform your teacher.

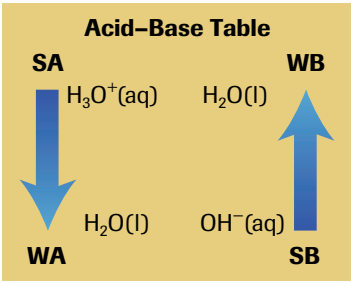


Figure 1
Simplified acid–base table

INVESTIGATION 16.2

Testing Brønsted–Lowry Reaction Predictions

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	● Materials	● Evaluation (1, 2, 3)
○ Hypothesis	● Procedure	
● Prediction	● Evidence	

When predicting products for this investigation, since at least one reactant is always in solution, list all entities present as they normally exist in an aqueous environment. For those reactants that are added in solid state, assume that they will dissolve. Use the resulting entities for prediction. Evaluate the predictions, the Brønsted–Lowry concept, and the five-step method for acid–base reaction prediction.

Purpose

The purpose of this investigation is to test the Brønsted–Lowry concept and the five-step method for reaction prediction from a table of relative acid–base strength.

Problem

What reactions occur when the following substances are mixed? (Hints for diagnostic tests are in parentheses.)

1. ammonium chloride and sodium hydroxide solutions (odour)
2. hydrochloric acid and sodium acetate solutions (odour)
3. sodium benzoate and sodium hydrogen sulfate solutions (benzoic acid has low solubility)
4. hydrochloric acid and aqueous ammonium chloride (odour)

INVESTIGATION 16.2 *continued*

5. solid sodium chloride added to water (litmus)
6. solid aluminium sulfate added to water (litmus)
7. solid sodium phosphate added to water (litmus)
8. solid sodium hydrogen sulfate added to water (litmus)
9. solid sodium hydrogen carbonate added to hydrochloric acid (pH)
10. solid sodium hydrogen carbonate added to sodium hydroxide solution (pH)
11. solid sodium hydrogen carbonate added to sodium hydrogen sulfate solution (pH)

Design

A prediction is made for each of eleven pairs of substances. The prediction is then tested using one or more diagnostic tests, complete with controls. Additional diagnostic tests increase the certainty of the evaluation.

Chemicals used include toxic, corrosive, and irritant materials. Avoid eye and skin contact. If you spill any of the chemical solutions on your skin, immediately rinse the area with lots of cool water. In the unlikely situation of getting some of the chemicals in your eye, immediately rinse your eye for at least 15 min and inform your teacher. Remember to detect odours cautiously by wafting air toward your nose from the container.

INVESTIGATION 16.3

Testing a Buffer Effect

References provide "recipes" for preparing standard buffer solutions of any desired pH from 1.0 to 13.0. The one used in this investigation has a pH of precisely 7.0, and might be used to calibrate a pH meter, for example. If our theory of buffers is correct, this solution should resist significant change in pH upon gradual addition of outside acid or base entities. Write the Design, Materials, and table of evidence to match the Procedure that is provided. The buffer is prepared by a reaction communicated by the following chemical equation:

$$\underset{\substack{\text{excess}\\\text{(acid part}\\\text{of buffer)}}}{H_2PO_4^-(aq)} + \underset{\substack{\text{limiting}\\\text{reagent}}}{OH^-(aq)} \longrightarrow \underset{\substack{\text{(base part}\\\text{of buffer)}}}{HPO_4^{2-}(aq)} + H_2O(l)$$

Purpose

The purpose of this investigation is to test our concept of buffers.

Problem

How does the pH change when a strong acid and a strong base are slowly added separately to an $H_2PO_4^-(aq)$–$HPO_4^{2-}(aq)$ buffer?

Acids and bases are corrosive and toxic. Avoid skin and eye contact. If you spill any of the chemical solutions on your skin, immediately rinse the area with lots of cool water. In the unlikely situation of getting some of the chemicals in your eye, immediately rinse your eye for at least 15 min and inform your teacher.

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	● Materials	● Evaluation (1, 2, 3)
○ Hypothesis	○ Procedure	
● Prediction	● Evidence	

Procedure

1. Obtain 50 mL of 0.10 mol/L $KH_2PO_4(aq)$ and 29 mL of 0.10 mol/L NaOH(aq) in separate graduated cylinders.
2. Pour the $KH_2PO_4(aq)$ and then the NaOH(aq) into a beaker to prepare a buffer with a pH of 7.
3. Pour an equal volume of the buffer into two test tubes.
4. Add 0.10 mol/L NaCl(aq) as a control into a third and a fourth test tube.
5. Add two drops of bromocresol green to one buffer test tube and one control test tube.
6. Add and count drops of 0.10 mol/L HCl(aq) until the colour changes.
7. Repeat steps 5 and 6 with phenolphthalein and 0.10 mol/L NaOH(aq) using the other two test tubes.
8. Dispose of all solutions down the drain with running water.

Chapter 16 SUMMARY

Outcomes

Knowledge

- describe Brønsted–Lowry acids as proton donors and bases as proton acceptors (16.2)
- write Brønsted–Lowry equations and predict whether reactants or products are favoured for acid–base equilibrium reactions (including indicators and polyprotic acids and bases) (16.2, 16.4)
- identify polyprotic acids, polyprotic bases, conjugate pairs, and amphiprotic entities (16.2, 16.4)
- define a buffer as relatively large amounts of a conjugate acid–base pair in equilibrium that maintain a relatively constant pH when small amounts of acid or base are added (16.4)
- sketch and qualitatively interpret titration curves of monoprotic and polyprotic acids and bases, identifying equivalence points and regions of buffering for weak acid–strong base, strong acid–weak base, and strong acid–strong base reactions (16.4)
- define K_w, K_a, and K_b and use them to determine pH, pOH, $[H_3O^+]$, and $[OH^-]$ of acidic and basic solutions (16.1, 16.3)
- calculate equilibrium constants and concentrations for homogeneous systems and Brønsted–Lowry acids and bases (excluding buffers) when concentrations at equilibrium are known, when initial concentrations and one equilibrium concentration are known, and when the equilibrium constant and one equilibrium concentration are known (16.1, 16.3)

STS

- state that the goal of science is knowledge about the natural world (16.1, 16.2, 16.3, 16.4)
- state that a goal of technology is to solve practical problems (16.2, 16.3, 16.4)

Skills

- initiating and planning: design an experiment to show quantitative equilibrium shifts in concentration under a given set of conditions (16.4); describe procedures for safe handling, storage, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (16.2, 16.4)
- performing and recording: prepare a buffer to investigate the relative abilities of a buffer and a control to resist a pH change when a small amount of strong acid or strong base is added (16.4)
- analyzing and interpreting: use experimental data to calculate equilibrium constants (16.3)
- communication and teamwork: work cooperatively in addressing problems and apply the skills and conventions of science in communicating information and ideas and in assessing results (16.2, 16.4)

Key Terms

16.1

ionization constant for water, K_w

16.2

Brønsted–Lowry acid

Brønsted–Lowry base

Brønsted–Lowry reaction equation

amphiprotic

amphoteric

conjugate acid–base pair

16.3

acid ionization constant, K_a

base ionization constant, K_b

16.4

pH curve

buffering

buffer

buffer capacity

Key Equations

(All at SATP)

$$K_w = [H_3O^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14} \quad (16.1)$$

$$pH + pOH = 14.00 \quad (16.1)$$

For any aqueous acid, HA(aq), $K_a = \dfrac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$ (16.3)

For any aqueous base, B(aq), $K_b = \dfrac{[HB^+(aq)][OH^-(aq)]}{[B(aq)]}$ (16.3)

For any conjugate acid–base pair, $K_aK_b = K_w$ (16.3)

MAKE a summary

1. Use a blank page to create a "star" (radial) chart for quantities and calculations related to Brønsted–Lowry acid–base reaction systems. Begin by writing $H_3O^+(aq)$ and $OH^-(aq)$ symbols about 10 cm apart horizontally, centred on the page and connected by a line. Draw lines from each of these symbols to other quantity symbols that are calculated from them (and from each other, in some cases). Along each connecting line, indicate what information the calculation requires and how it is performed. Include K_a, K_b, pH, and pOH quantities, but not percent ionization (because it is not specific to acid–base reactions).
2. Revisit your answers to the Starting Points questions at the beginning of this chapter. How would you answer the questions differently now? Why?

Go To

www.science.nelson.com GO

The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 16
- additional Diploma Exam-style Review questions
- Illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

EXTENSION

Lost Treasures of Tibet

What does acid–base chemistry have to do with ancient works of art? Watch this video to discover how archeologists and conservators made use of chemical reactions to restore the brilliance to Tibetan temple paintings.

www.science.nelson.com GO

Chapter 16 REVIEW

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

www.science.nelson.com GO

DO NOT WRITE IN THIS TEXTBOOK.

Part 1

1. A hydrated proton is referred to as a
   A. hydronium ion
   B. hydroxide ion
   C. hydroxyl group
   D. Brønsted–Lowry base

2. The hydroxide ion concentration in a solution of window cleaner is 2.1 mmol/L. The hydronium ion concentration in this solution is calculated to be
   A. 2.1×10^{-15} mol/L
   B. 4.8×10^{-15} mol/L
   C. 2.1×10^{-12} mol/L
   D. 4.8×10^{-12} mol/L

3. A pH meter indicates that the pH of a soft drink is 3.46. The pOH of the soft drink is calculated to be
   A. 10.46
   B. 10.54
   C. 14.46
   D. 14.54

4. The recipe for preparing a cleaning solution calls for dissolving 5.0 g of sodium hydroxide in 4.0 L of water. The pH of the resulting solution is calculated to be
   A. 1.51
   B. 12.49
   C. 13.10
   D. 13.90

5. Acid–base theories have developed over the last two centuries. Which of the following chemists did *not* make a significant contribution to acid–base theory?
   A. Gilbert Lewis
   B. Svante Arrhenius
   C. Ernest Rutherford
   D. Johannes Brønsted

Use the names given and Appendix G to answer questions 6 and 7. Note that some of the ions listed are amphiprotic.
1. phenol
2. sulfide ion
3. cyanide ion
4. ammonium ion
5. hydrogen sulfate ion
6. hydrogen carbonate ion

6. Listed from strongest to weakest, the acids are NR ___ ___ ___ ___.

7. Listed from strongest to weakest, the bases are NR ___ ___ ___ ___.

8. The nearly level region on a pH curve represents
   A. the endpoint
   B. a region of buffering
   C. an indicator point
   D. the equivalence point

9. The titration of a weak acid with a strong base has an equivalence point pH of 9.0. Which of the following indicators would be most suitable for this titration, done as an analysis?
   A. litmus
   B. methyl red
   C. phenolphthalein
   D. alizarin yellow R

10. Which of the following combinations of ions does *not* represent a conjugate acid–base pair?
   A. $H_3PO_4(aq)$ and $H_2PO_4^-(aq)$
   B. $H_2PO_4^-(aq)$ and $HPO_4^{2-}(aq)$
   C. $HPO_4^{2-}(aq)$ and $PO_4^{3-}(aq)$
   D. $H_3PO_4(aq)$ and $HPO_4^{2-}(aq)$

11. Which of the following statements about acid–base titrations is *not* true?
   A. Strong acid–strong base reactions have an equivalence point pH of 7.
   B. Strong acid–weak base reaction equivalence points have a pH > 7.
   C. Weak acid–strong base reaction equivalence points have a pH > 7.
   D. Strong acid–strong base reactions are quantitative.

12. Which of the following statements about buffers is *not* true?
   A. Buffers maintain a solution pH at approximately 7.
   B. Buffers can be formed by partially neutralizing a weak acid with a strong base.
   C. Buffers maintain a relatively constant pH when small amounts of acid or base are added.
   D. Buffers contain relatively large amounts of a conjugate acid–base pair in equilibrium.

Part 2

13. **Define** each of the following substances, according to the Brønsted–Lowry theory.
(a) an acid
(b) a base
(c) an acid–base reaction
(d) an amphiprotic entity
(e) a strong acid
(f) a strong base

14. Write net ionic equations for each of the following reactions in aqueous solution. Label the reactants as Brønsted–Lowry acids or bases. **Identify** any amphiprotic ions.
(a) Solutions of sodium hydrogen sulfate and sodium carbonate are mixed.
(b) Aqueous ammonia is added to a solution of potassium hydrogen sulfite.
(c) Solutions of sodium hydrogen phosphate and acetic acid are mixed.
(d) Aqueous sodium hydroxide is added to a solution of sodium hydrogen phosphate.

15. **Identify** all acids, bases, and conjugate pairs, and **predict** the position of equilibrium (reactants or products favoured) in each of the following reactions.
(a) $CH_3COOH(aq) + CN^-(aq) \rightleftarrows CH_3COO^-(aq) + HCN(aq)$
(b) $HSO_3^-(aq) + HPO_4^{2-}(aq) \rightleftarrows SO_3^{2-}(aq) + H_2PO_4^-(aq)$
(c) $NH_4^+(aq) + CO_3^{2-}(aq) \rightleftarrows NH_3(aq) + HCO_3^-(aq)$

16. Write equilibrium law expressions for each of the following equilibrium situations.
(a) $HF(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + F^-(aq)$
(b) $NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$
(c) $H_2SO_3(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + HSO_3^-(aq)$

17. Refer to Appendix I for required information to **predict** $[H_3O^+(aq)]$ and pH for each of these 0.10 mol/L solutions.
(a) hydroiodic acid
(b) methanoic acid (optional: enrichment)
(c) hydrosulfuric acid

18. A student measures the pH of a 0.25 mol/L solution of potassium hydrogen citrate to be 3.42.
DE
(a) **Determine** the K_a of the hydrogen citrate ion from this evidence.
(b) How could a student find the pH of a solution without access to a pH meter? **Design** a procedure, involving three indicators, that would establish the approximate pH of this solution. **Criticize** your design.

19. If a sample of acid rain has a pH of 5.0, **predict** the colour of each of the following indicators in this solution.
(a) litmus
(b) methyl red
(c) methyl orange
(d) phenolphthalein

20. Aqueous 0.10 mol/L solutions of potassium sulfate and potassium benzoate are prepared. **Predict** how the pH values of the solutions would compare, using the Brønsted–Lowry proton transfer concept to **justify** your answer.

21. Separate samples of a household cleaning solution were tested with two indicators. Indigo carmine was blue and phenolphthalein was red in the solution. Estimate the approximate pH and approximate hydroxide ion concentration in the solution.

22. **Determine** the percent reaction, pH, pOH, and hydroxide concentration in a 0.015 mol/L solution of sodium acetate.

23. **Sketch** a pH (titration) curve for each of the following titrations, assuming all the acids and bases have a concentration of 0.10 mol/L, and all reaction proton transfers are quantitative.
(a) A diprotic acid is titrated with sodium hydroxide.
(b) A diprotic base is titrated with hydrochloric acid.

24. **Design** an experiment to determine the relative strengths of four weak acids.

25. Use the five-step Brønsted–Lowry method to **predict** the net ionic equation for the overall reaction when the following chemicals are mixed.
(a) solutions of sodium sulfate and potassium benzoate
(b) aqueous ammonium nitrate fertilizer and aqueous sodium phosphate
(c) solutions of citric acid and sodium hydrogen carbonate

Unit 8 REVIEW

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

www.science.nelson.com GO

DO NOT WRITE IN THIS TEXTBOOK.

Part 1

1. The following aqueous solutions are each at equilibrium in sealed containers that are half-full of liquid. For which one of these may the volume of the liquid solution be reasonably considered to be the boundary of the closed system for the equilibrium?
A. HCl(aq)
B. NaOH(aq)
C. $H_2CO_3(aq)$
D. $NH_3(aq)$

2. Basicity of solutions has been explained by a variety of theories, each one more comprehensive than its predecessors. The Brønsted–Lowry concept defines a base as an entity that is a
A. proton attractor in a specific acid–base reaction
B. proton donor in a specific acid–base reaction
C. hydronium attractor in any acid–base reaction
D. hydroxide producer in any acid–base reaction

3. For which of the following aqueous solution titrations would you expect to measure a pH of 7 at the equivalence point, at SATP?
A. acetic acid titrated with sodium hydroxide
B. nitric acid titrated with potassium carbonate
C. hydrochloric acid titrated with lithium hydroxide
D. ammonia titrated with hydrochloric acid

4. An industrial reaction process designer has a choice of several different equilibrium reactions, all of which produce the same desired chemical substance. These reactions each have different reaction characteristics. The designer wishes to produce product as fast as is safely possible. The best choice from an economic perspective is the reaction that
A. has a high rate (speed) of reaction and a low percent yield
B. has a low rate (speed) of reaction and a high percent yield
C. requires extreme high pressure to improve the percent yield
D. requires an expensive catalyst to react noticeably

5. What energy condition must be met to maintain a dynamic equilibrium system?
A. The temperature must be constant.
B. The forward reaction must be exothermic.
C. The container must not conduct heat.
D. The activation energy must be high.

Use this information to answer questions 6 to 8.

Pure solid arsenic acid, also called orthoarsenic acid, is a hydrated substance at room temperature with a formula that may be written as $H_3AsO_4 \cdot \frac{1}{2}H_2O(s)$, or alternatively as $(H_3AsO_4)_2 \cdot H_2O(s)$. This substance is used in commercial glassmaking and in making wood-preservative solutions. Arsenic acid is soluble in water and ionizes according to the following equation:

$$H_3AsO_4(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + H_2AsO_4^-(aq)$$
$$K_a = 5.6 \times 10^{-3} \quad (18\ ^\circ C)$$

6. The conjugate base of arsenic acid in the ionization reaction shown is
A. $H_3AsO_4(aq)$
B. $H_2AsO_4^-(aq)$
C. $HAsO_4^{2-}(aq)$
D. $AsO_4^{3-}(aq)$

7. Which is the correct form of the equilibrium law for this acid ionization reaction?

A. $K_a = \dfrac{[H_3O^+(aq)][H_2AsO_4^-(aq)]}{[H_3AsO_4(aq)]}$

B. $K_a = \dfrac{[H_3O^+(aq)][H_2AsO_4^-(aq)]}{[H_3AsO_4(aq)][H_2O(aq)]}$

C. $K_a = \dfrac{[H_3O^+(aq)]}{[H_3AsO_4(aq)][H_2AsO_4^-(aq)]}$

D. $K_a = \dfrac{[H_3O^+(aq)][H_2AsO_4^-(aq)]}{[H_3AsO_4(aq)][HAsO_4^{2-}(aq)]}$

8. An empirical pH curve for a titration of a sample of aqueous arsenic acid with a standardized sodium hydroxide solution shows two distinct rapid changes in pH. From this evidence, it can be inferred that
A. hydrogen arsenate ion is a very weak acid, with a relatively strong conjugate base
B. arsenate ion is a very weak base, with a strong conjugate acid
C. an arsenic acid molecule can lose two protons simultaneously to one hydroxide ion
D. the third sequential proton transfer reaction is quantitative

9. NR A student discovers that a pure liquid substance that is sold as a common agricultural insecticide forms an acidic solution in water. The measured pH of a 1.00 mol/L aqueous solution of this weak acid is 5.22. The calculated K_a value for this acid at this temperature may be expressed numerically as $a.b \times 10^{-cd}$. The values (in order) of *a*, *b*, *c*, and *d* are _____, _____, _____, and _____.

10. In writing an equilibrium law expression, condensed (pure solid and liquid) phases are ignored because
    A. forward and reverse reaction rates must be equal if they occur at the surface of a solid or liquid
    B. solids and liquids are completely separate physically from the rest of the reaction components, which are dissolved in each other
    C. solid or liquid pure substances have essentially constant amount concentration values
    D. other entities cannot move between molecules of solids or liquids to collide with their entities

11. Consider the reaction $N_2(g) + 3\ H_2(g) \rightleftarrows 2\ NH_3(g)$, at equilibrium. If the system container volume were to be suddenly decreased, the concentration of nitrogen gas in the system would immediately
    A. increase, then decrease to a new constant value
    B. remain unchanged, because the reaction is at equilibrium
    C. increase, then remain steady at a new constant value
    D. decrease, then remain steady at a new constant value

Use this information to answer questions 12 to 14.

Titration of acid samples with hydroxide ion solution produces very different pH curves depending on the strength of the acid sample (**Figure 1**). These curves represent data from two separate titrations plotted on the same axes. The two acid samples were standardized hydrochloric acid and acetic acid solutions, both with the same initial concentration and volume. The same sodium hydroxide titrant was used in both titrations.

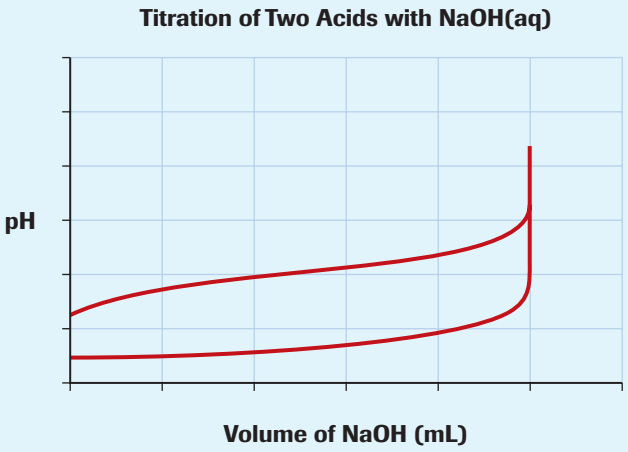


Figure 1
Titration curves for HCl(aq) and $CH_3COOH(aq)$ with NaOH(aq)

12. The strong acid titration curve does not increase noticeably when the very *first* addition of NaOH(aq) is made, because
    A. $OH^-(aq)$ was already present in the original sample solution
    B. $OH^-(aq)$ does not initially react with entities present in the sample solution
    C. reaction of the added $OH^-(aq)$ creates no new entities in the sample solution
    D. hydronium ions resist any change to their structure

13. During most of these titrations, the pH curves remain nearly level. The conjugate acid–base pair that is responsible for creating this buffering region during the strong acid–strong base titration is
    A. $H_3O^+(aq) - H_2O(l)$
    B. $H_3O^+(aq) - CH_3COOH(aq)$
    C. $CH_3COOH(aq) - CH_3COO^-(aq)$
    D. $CH_3COO^-(aq) - OH^-(aq)$

14. The *incorrect* statement about the weak acid–strong base titration is:
    A. Initial addition of $OH^-(aq)$ produces a new entity in the sample solution.
    B. The titrant volume at the reaction equivalence point is the same as for the strong acid–strong base titration.
    C. The solution pH at the reaction equivalence point will be higher than for the strong acid–strong base titration.
    D. At the equivalence point, the solution pH will be controlled by the concentration of hydroxide ion, which is the strongest base present.

Part 2

15. Formal concepts of acids have existed since the 18th century. **Explain** the main idea and the limitations of each of the following: the oxygen concept; the hydrogen concept; Arrhenius' concept; and the Brønsted–Lowry concept of acids.

16. What happens when scientists find a theory, such as Arrhenius' original theory of acids, to be unacceptable?

17. **Describe** two main ways in which a theory or a theoretical definition may be tested, in terms of what an *acceptable* theory is required to do.

18. According to modern evidence, what is the nature of a "hydrogen ion" in aqueous solution?

19. Briefly **outline** how the theoretical definition of a base has changed from Arrhenius' original concept to the modified Arrhenius concept, and subsequently to the Brønsted–Lowry concept.

20. Aqueous solutions of sodium sulfite and of sodium carbonate of equal concentrations are prepared. **Explain** how the pH values would compare, using the Brønsted–Lowry proton transfer concept to **justify** your answer.

21. Use the *If* [procedure], *and* [evidence], *then* [analysis] format (Appendix C.4) to **describe** a diagnostic test that could be used to determine which of two solutions (of equal concentration) is sodium benzoate, and which is sodium hydroxide.

22. **Identify** two different examples of conjugate acid–base pairs, each involving the dihydrogen phosphate ion.

23. Which of the following statements are necessarily true when products are strongly favoured in an acid–base equilibrium, assuming equal amount concentrations and chemical amounts of the initial reactants?

(a) The stronger of the two Brønsted–Lowry bases is a product.
(b) The equilibrium constant is greater than one.
(c) The forward reaction is exothermic.
(d) The stronger Brønsted–Lowry acid is a reactant.
(e) The percent reaction is greater than 50%.
(f) The pH of the final solution is greater than 7.
(g) The reactant acid is above the reactant base in an acid–base table.

24. From the equation information provided, **predict** all of the system changes you might introduce that, according to Le Châtelier's principle, will act to shift the equilibria to maximize the percent yield of the specified product.

(a) production of propene (propylene)
$C_3H_8(g) + \text{energy} \rightleftarrows C_3H_6(g) + H_2(g)$
(b) production of iodine
$5\ Sn^{2+}(aq) + 2\ IO_3^-(aq) + 12\ H_3O^+(aq) \rightleftarrows 5\ Sn^{4+}(aq) + I_2(s) + 18\ H_2O(l)$

25. Consider this system at equilibrium.
$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$; $K_c = 0.40$ at 170 °C

(a) One mole of phosphorus pentachloride was initially placed into a 1.0 L container. Once equilibrium had been reached, it was found that the equilibrium concentration of PCl_5 was 0.54 mol/L. **Figure 2** describes the change in $[PCl_5]$ over time. Copy the graph. **Sketch** lines to indicate the changing concentrations of PCl_3 and Cl_2 over the same time period.

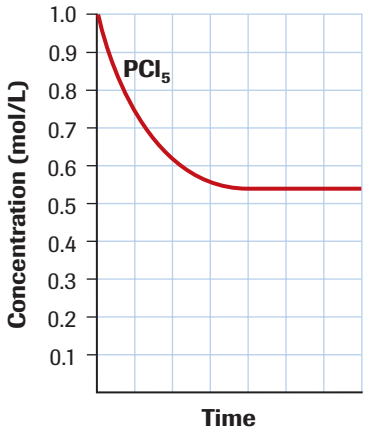


Figure 2
Reaction progress: $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$

(b) 0.50 mol of PCl_3 and 0.30 mol of Cl_2 were placed into a 1.0 L container. Once equilibrium had been reached, it was found that the equilibrium concentration of PCl_3 was 0.36 mol/L. **Figure 3** describes the change in $[PCl_3]$ over time. Copy the graph. **Sketch** how the concentrations of PCl_5 and Cl_2 change over the same time period.

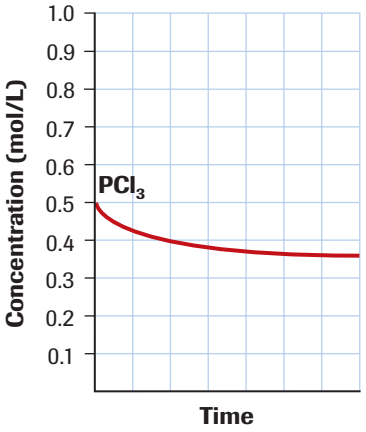


Figure 3
Reaction progress: $PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g)$

26. Consider the equilibrium reaction,
$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$ $K_c = 5.0$ at 650 °C
In a rigid 1.00 L laboratory reaction vessel, a technician places 1.00 mol of each of the four substances involved in this equilibrium. The vessel is heated to 650 °C.
Determine the equilibrium amount concentrations of each substance, organizing your values in an ICE table.

27. Write chemical formulas and net ionic equations for the following overall reactions. (If necessary, refer to Appendix J.)

(a) Vinegar is used to neutralize a drain cleaner spill.
(b) Baking soda solution is used to neutralize spilled rust remover containing oxalic acid.
(c) An antacid tablet (flavoured calcium carbonate) is used to neutralize excess stomach acid.

28. Identify all acids, bases, and conjugate pairs, and **predict** the position of equilibrium (reactants or products favoured) in each of the following reactions:

(a) $HCOOH(aq) + CN^-(aq) \rightleftarrows HCOO^-(aq) + HCN(aq)$
(b) $HPO_4^{2-}(aq) + HCO_3^-(aq) \rightleftarrows H_2PO_4^-(aq) + CO_3^{2-}(aq)$
(c) $Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + Al(H_2O)_5OH^{2+}(aq)$
$K_a = 1 \times 10^{-5}$
(d) $C_6H_5NH_2(aq) + H_2O(l) \rightleftarrows C_6H_5NH_3^+(aq) + OH^-(aq)$
$K_b = 4 \times 10^{-10}$

29. Separate samples of an unknown solution were tested with two indicators. Congo red was red and chlorophenol red was yellow in the solution. **Predict** the approximate pH and approximate hydronium ion concentration of the solution.

30. The test for acceptability of any theory is its ability to explain and predict a wide range of phenomena: to be a unifying theory. Test the Brønsted–Lowry concept by using the five-step procedure to write chemical equations describing and predicting each of the following acid–base reactions. **Design**, where possible, one diagnostic test that could be used to verify each prediction.

(a) the addition of hydrofluoric acid to a solution of potassium sulfate
(b) the addition of a solution of sodium hydrogen sulfate to a solution of sodium hydrogen sulfide
(c) the titration of methanoic acid with sodium hydroxide solution
(d) the addition of a small amount of a strong acid to a hydrogen phosphate ion–phosphate ion buffer solution
(e) the addition of colourless phenolphthalein indicator, HPh(aq), to a strong base
(f) sodium sulfate is dissolved in water
(g) the addition of blue bromothymol blue, $Bb^-(aq)$, to vinegar
(h) the addition of washing soda to water
(i) the addition of baking soda to water

31. DE Many acid–base phenomena can be described and/or predicted by using Le Châtelier's principle. **Evaluate** this generalization's ability to describe or predict a variety of reactions.

Your response should include

- reference to the following three examples:
  NaOH(aq) is added to the following buffer equilibrium:
  $NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$
  NaOH(aq) is added to a bromothymol blue indicator solution:
  $HBb(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + Bb^-(aq)$
  NaOH(aq) titrant is added to a vinegar sample:
  $CH_3COOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$
- descriptions of diagnostic tests that would provide evidence for your predictions

32. One way to evaluate a theory is to test predictions with new substances. Sodium methoxide, $NaCH_3O(s)$, is dissolved in water. **Predict** whether the final solution will be acidic, basic, or neutral. **Explain** your answer using a net ionic equation. (Hint: Think of the methoxide ion as a hydroxide ion, with a methyl group substituted for the hydrogen.)

33. DE In an experimental investigation of amphoteric substances, samples of baking soda were added to a solution of sodium hydroxide and to a solution of hydrochloric acid. The pH of the sodium hydroxide changed from 13.0 to 9.5 after the addition of the baking soda. The pH of the hydrochloric acid changed from 1.0 to 4.5 after the addition of baking soda. **Explain** these results.

Your response should include

- chemical reaction equations to describe the reactions
- identification of the amphiprotic entity

34. Each of seven unlabelled beakers was known to contain one of the following 0.10 mol/L solutions: $CH_3COOH(aq)$, $Ba(OH)_2(aq)$, $NH_3(aq)$, $C_2H_4(OH)_2(aq)$, $H_2SO_4(aq)$, HCl(aq), and NaOH(aq). **Describe** diagnostic test(s) required to distinguish the solutions and label the beakers. Use the "*If* ____, *and* ____, *then* ____" format (Appendix C.4), a flow chart, or a table to communicate your answer.

35. Use **Figure 4** to answer the following questions.

DE (a) **Infer** how many quantitative reactions have occurred.
(b) Write the Brønsted–Lowry equation for each successive proton transfer reaction, with appropriate "arrows" to indicate the extent of each reaction.
(c) **Determine** the titrant volume at each quantitative reaction equivalence point.
(d) **Identify** a suitable indicator to correspond to the equivalence point pH values.
(e) **Identify** the buffering region(s), and state the chemical formulas for the entities present in solution in each buffering region.

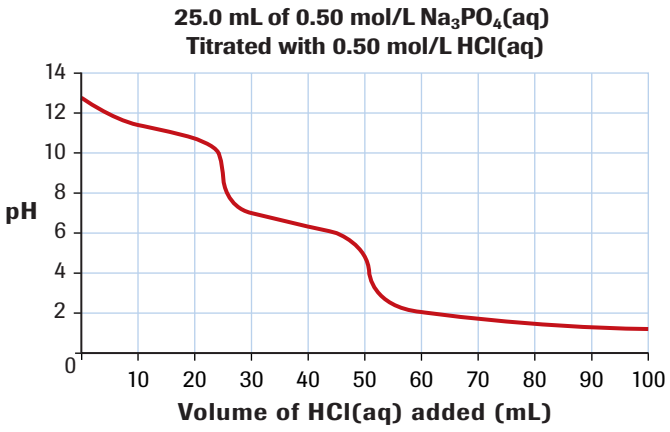


Figure 4
Graph for question 35

36. Because chlorine–oxygen compounds are toxic to micro-organisms and react readily with organic materials in food stains, they find wide application in disinfectants and bleaches. The reaction of hypochlorous acid with molecules of coloured substances in stains often produces colourless products, making the stain "disappear." Hypochlorous acid may be produced by the following reaction:
$H_2O(g) + Cl_2O(g) \rightleftarrows 2\,HOCl(g)$
$K_c = 0.090$ (25 °C)
Determine the concentrations of each reagent at equilibrium at 25 °C if the initial concentrations of both water vapour and chlorine monoxide were 4.00 mol/L.

37. Ethyl acetate (ethyl ethanoate) is an ester with a great many different uses as an organic solvent—for everything from paint to perfume. It is a product of the following equilibrium reaction equation:

$$CH_3COOH(os) + C_2H_5OH(os) \rightleftarrows CH_3COOC_2H_5(os) + H_2O(os)$$

The equation shows the reaction taking place at 25 °C, with all components dissolved in a complex non-reacting liquid organic solvent, which we have symbolized as "os" for convenience. **Determine** K_c for this reaction if, at equilibrium, the reagent concentrations are

$[CH_3COOH(os)] = 2.5$ mol/L
$[C_2H_5OH(os)] = 1.7$ mol/L
$[CH_3COOC_2H_5(os)] = 3.1$ mol/L
$[H_2O(os)] = 3.1$ mol/L

38. Phenolphthalein indicator was used for a titration of several 10.00 mL samples of hypochlorous acid with 0.350 mol/L barium hydroxide solution. An average titrant volume of 12.6 mL was required to reach the observed endpoint of these trials. According to this evidence, **predict** the amount concentration of the hypochlorous acid solution.

39. DE In a titration, 0.20 mol/L HCl(aq) titrant is to be gradually added to a 20.0 mL sample of 0.10 mol/L NaOH(aq).

(a) **Sketch** a theoretical (calculated) pH curve.
(b) Include the following information as labels on your sketch. Show all relevant calculations.
  (i) the equivalence point pH and titrant volume for the reaction
  (ii) the initial pH of the sodium hydroxide sample solution
  (iii) the pH after adding 5.0 mL of HCl(aq) (treat this part as a limiting reagent calculation)
  (iv) the entities present at the equivalence point
  (v) the pH after adding 9.0 mL of HCl(aq)
  (vi) the pH after adding 11.0 mL of HCl(aq)
(c) Suggest a suitable indicator for an endpoint determination for this titration. Indicate the pH values for the indicator colour change range on your pH curve.

Use this information to answer questions 40 to 43.

Lime is a very simple substance, and very easily prepared by strongly heating natural chalk. It has been used throughout recorded history, and by now the word "lime" appears in common names for many substances. Lime is calcium oxide, CaO(s), which is often sold as quicklime, or unslaked lime. This oxide is hazardous to handle because it reacts very readily and rapidly with water, releasing a lot of heat. When "slaked" with water, it forms calcium hydroxide, $Ca(OH)_2(s)$, which is much less dangerous to handle. This compound is widely sold in garden stores as agricultural, or horticultural, lime—meaning a rather impure form. It is commonly added to soils to raise the soil pH value, because the absorption by plants of some nutrients and trace elements depends heavily on soil pH levels.

Hydrochloric acid has also been in common use for a very long time. It is still sold under its historical name, muriatic acid, usually as a solution of about 30–35% HCl. It is very useful as a powerful rust remover, or to adjust pH levels in swimming pools. It will also "etch" the surface of concrete by reacting with carbonate ions in the solid mixture, with the result that paint can adhere to the clean, rough concrete surface. A spill of this very corrosive acid is always a serious problem (**Figure 5**).

Figure 5
Horticultural lime (calcium hydroxide) is quickly sprinkled on a spill of concentrated muriatic (hydrochloric) acid.

40. DE The solubility of calcium hydroxide is expressed in the following equation, representing a saturated solution equilibrium at 25 °C:

$$Ca(OH)_2(s) \rightleftarrows Ca^{2+}(aq) + 2\ OH^-(aq)$$
$$K_c = 1.3 \times 10^{-6}$$

(a) **Predict** whether calcium hydroxide is highly soluble or only slightly soluble in water.
(b) What is the common name for a saturated calcium hydroxide solution, and what diagnostic test can be performed with it?
(c) **Explain** how the solubility makes this compound safe to handle, even though hydroxide ion is the strongest base possible in aqueous solution.
(d) **Explain** why "liming" of a (moist) garden soil will only raise the pH by a small amount, but then will continue to keep it elevated for months.

41. In a concentrated commercial hydrochloric acid solution, about one of every four molecules is HCl, as calculated from the mass percent printed on the label. **Predict** what fraction of these HCl molecules is actually in the "ready to react" form of $H_3O^+(aq)$.

42. When neutralizing this acid spill with calcium hydroxide, **identify** which compound you would want to be in excess, and **explain** why.

43. Write a chemical equation and a Brønsted–Lowry equation for this neutralization.

44. DE A series of experiments with a non-aqueous solvent determined that the products are highly favoured in each of the following acid–base equilibria, as written.

$(C_6H_5)_3C^- + C_4H_4NH \rightleftarrows (C_6H_5)_3CH + C_4H_4N^-$

$CH_3COOH + HS^- \rightleftarrows CH_3COO^- + H_2S$

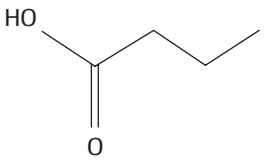
$O^{2-} + (C_6H_5)_3CH \rightleftarrows OH^- + (C_6H_5)_3C^-$

$C_4H_4N^- + H_2S \rightleftarrows C_4H_4NH + HS^-$

(a) Identify the Brønsted–Lowry acids, bases, and conjugate acid–base pairs in each of these chemical reactions.

(b) Arrange the acids in these four chemical reactions in order of decreasing acid strength (in the solvent used), as a standard table of acids and conjugate bases.

45. The hydronium ion concentration of a 0.100 mol/L *n*-butanoic (butyric) acid solution was measured to be 1.24×10^{-3} mol/L.



Determine the percent reaction (ionization) of this particular weak acid solution, and a K_a value for aqueous *n*-butanoic acid at this ambient temperature.

46. A 0.10 mol/L solution of the essential amino acid tryptophan (1-α-amino-3-indolepropanoic acid) has a measured pH of 5.19 at 25 °C. **Predict** the percent reaction of this tryptophan solution, and the K_a value for aqueous tryptophan. The molecular formula for tryptophan may be written as $C_{10}H_{11}N_2COOH$.

47. Glycine, $H_2NCH_2COOH(aq)$, is a nonessential amino acid, with the simplest structure of all the amino acids, and has a $K_a = 4.5 \times 10^{-7}$ at 25 °C. Calculate the hydronium ion concentration, the pH, and the percent reaction in a 0.050 mol/L aqueous solution of glycine at 25 °C.

48. DE Thioacetic acid, $CH_3COSH(aq)$, has a $K_a = 4.7 \times 10^{-4}$ at 25 °C.

(a) Write the K_a expression for thioacetic acid.

(b) Calculate the hydronium and thioacetate ion concentrations, the pH, and the percent reaction in a 2.00 mol/L $CH_3COSH(aq)$ solution at 25 °C.

(c) Calculate K_b for the conjugate base, the thioacetate ion.

49. **Predict** the percent reaction, pH, pOH, and hydroxide ion concentration of a 0.012 mol/L solution of sodium benzoate.

50. A 0.100 mol/L laboratory solution of sodium propanoate, $NaC_2H_5COO(aq)$, has a measured pH of 8.95 at 25 °C. Calculate K_b for the propanoate ion.

51. DE Chloro-substituted acetic acids are used in organic synthesis, cleaners, and herbicides. These acids are prepared by the chlorination of acetic acid in the presence of small amounts of phosphorus. This process is known as the Hell–Volhard–Zelinsky reaction. As is typical of organic synthesis reactions, at equilibrium, the reaction vessel contains a mixture of all the different possible reaction products as well as some unreacted acetic acid and chlorine. When these acids were studied separately, the data in **Table 1** were obtained.

Table 1 Comparison of 0.100 mol/L Solutions of Acetic Acid and the Chloroacetic Acids

Substance	Formula	pH
acetic acid	$CH_3COOH(aq)$	2.89
chloroacetic acid	$CH_2ClCOOH(aq)$	1.94
dichloroacetic acid	$CHCl_2COOH(aq)$	1.30
trichloroacetic acid	$CCl_3COOH(aq)$	1.14

(a) Calculate acid ionization constants for each chloroacetic acid. Write chemical equations to describe the reactions of these acids with water.

(b) Suggest a theoretical explanation for the relative strengths of this series of acids. (Hint: Would adding chlorines to the *other* end of the molecule make the –COOH end of the molecule more, or less, negative?)

(c) A chemical technician is assigned the design of an acid–base titration to determine the amounts of each acid present in the mixture. She knows from experience that the reaction of acetic acid with a strong base is quantitative. **Sketch** a simplified pH curve for titration of a mixture of the four acids produced by chlorinating acetic acid. How could the technician determine relative chemical amounts of the acids present in the mixture?

52. DE Liquid ammonia can be used as a solvent for acid–base reactions.

(a) **Predict** the strongest acid entity that could be present in this solvent. (Consider the parallel with liquid water, $H_2O(l)$. Also consider the likely reaction of a very strong proton donor, such as hydrogen chloride, when it dissolves and reacts quantitatively in liquid ammonia.)

(b) The ionization equilibrium of pure liquid ammonia is similar to that of pure liquid water. Write the equilibrium equation for the ionization of liquid ammonia.

(c) **Predict** the strongest base that could be present in liquid ammonia solution.

(d) **Sketch** a titration curve for the addition of the strongest acid in ammonia solution to the strongest base. Suggest what value, instead of pH, might be used on the vertical axis of your graph.

53. Review the focusing questions on page 670. Using the knowledge you have gained from this unit, briefly **outline** a response to each of these questions.